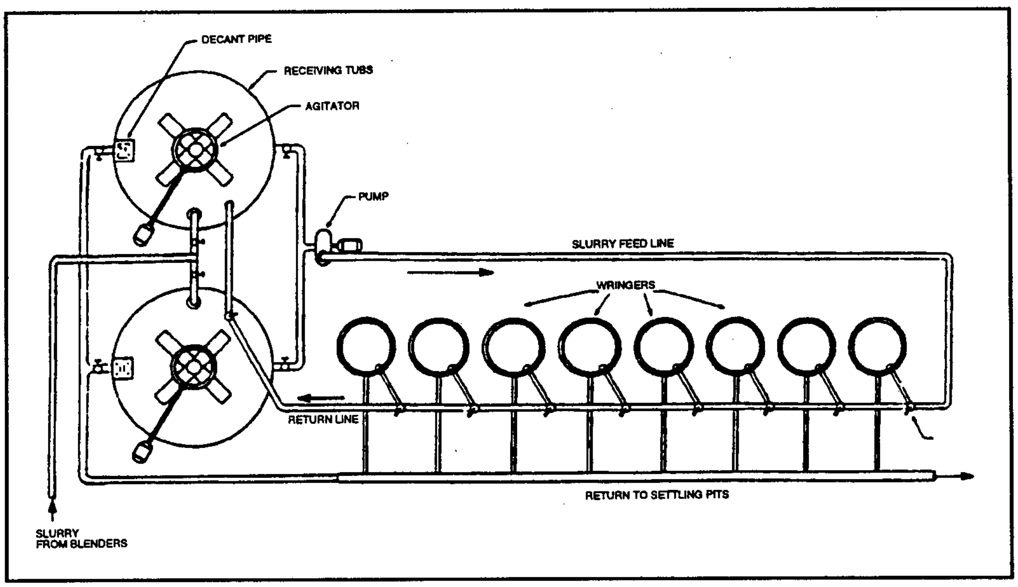
US Army Corps
of Engineers
Construction Engineering
Research Laboratories

USACERL Technical Report 97/138
September 1997

Characterization of Nitrocellulose Fines in Wastewater and Development of Pollution Prevention Strategy

by
Byung J. Kim, James K. Park, and Lee W. Clapp



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The U.S. Army Construction Engineering Research Laboratories (USACERL) has been evaluating technical alternatives and developing technologies to separate, recycle, and treat NC fines from RAAP manufacturing wastewater. This study characterized the physical properties of NC fines and developed a strategy to prevent pollution with NC fines. Characterized parameters included particle size distribution (PSD), total suspended solids (TSS), turbidity, zeta potential (particle surface charge), conductivity, and pH. Recommended pollution prevention methods included separation and recycle of NC fines at each process, more effective settling, and in-process modifications.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave Blank)*

2. REPORT DATE
September 1997

3. REPORT TYPE AND DATES COVERED
Final

4. TITLE AND SUBTITLE
Characterization of Nitrocellulose Fines in Manufacturing Wastewater and Development of Pollution Prevention Strategy

5. FUNDING NUMBERS
4A162720
D048
TE5

6. AUTHOR(S)
Byung J. Kim, James K. Park, and Lee W. Clapp

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Construction Engineering Research Laboratories (USACERL)
P.O. Box 9005
Champaign, IL 61826-9005

8. PERFORMING ORGANIZATION REPORT NUMBER
TR 97/138

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Headquarters, U.S. Army Corps of Engineers (HQUSACE)
ATTN: SFIM-AEC-ET
20 Massachussetts Ave., NW
Washington, DC 29314-1000

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Copies are available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS
nitrocellulose fines
wastewater treatment systems
pollution prevention

15. NUMBER OF PAGES
80

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	SAR

Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers (HQUSACE) under Project 4A162720D048, "Industrial Operations Pollution Control Technology"; Work Unit TE5, "Nitrocellulose Fines Abatement." The technical monitor was Gene Fabian, SFIM-AEC-ET.

The work was performed by the Industrial Operations Division (UL-I) of the Utilities and Industrial Operations Laboratory (UL), U.S. Army Construction Engineering Research Laboratories (USACERL). The USACERL principal investigator was Dr. Byung J. Kim. Dr. James Park is an associate professor and Lee Clapp is a graduate student at the University of Wisconsin at Madison. Walter J. Mikucki is Chief, CECER-UL-I; John T. Bandy is Operations Chief, CECER-UL; and Gary W. Schanche is the associated Technical Director, CECER-UL. The USACERL technical editor was William J. Wolfe, Technical Resources.

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1 Introduction

Background

Radford Army Ammunition Plant (RAAP), VA is the only Government owned, active munitions-grade nitrocellulose (NC) manufacturing facility in the United States. Various NC manufacturing processes at RAAP produce wastewater that contains NC particles in millimeter range as well as in the micron and sub-micron range, which are referred to as NC fines. RAAP generates about 2,000 lb per day of NC fines in its NC manufacturing process wastewater at full operation. Under U.S. Army Environmental Quality Technology (Compliance Pillar) Research and Development (R&D) program, the U.S. Army Construction Engineering Research Laboratories (USACERL) has been evaluating technical alternatives and developing technologies to separate, recycle, and treat the NC fines from the RAAP manufacturing wastewater.

Although some NC fines characterization data have been available, these data vary widely and often conflict each other, because most are based on "grab samples," in which the wastewater quality can fluctuate widely depending on unit operations and batch operation sequence. Therefore, there is a critical need to collect and analyze NC fines size distribution, concentration, and other NC fines characteristics at each sequence for each unit operation over an extended period of time.

Objectives

The objectives of this study were to characterize the physical properties of NC fines and to develop a strategy to prevent pollution with NC fines. The parameters to be characterized included particle size distribution (PSD), total suspended solids (TSS), turbidity, zeta potential (particle surface charge), conductivity, and pH. Pollution prevention methods considered included separation and recycle of NC fines at each process, more effective settling, and in-process modifications.

Approach

Field data were collected over an extended time period. (A team from the University of Wisconsin at Madison (UW) visited RAAP for 2 weeks and collected data at each sequence of each unit operation.) At least two sets of field data were collected and additional samples were analyzed at the Department of Civil and Environmental Engineering Laboratory, UW. Chapter 3 details the techniques used to define the desired wastewater characteristics.

The PSD and TSS concentrations were measured in the various NC manufacturing wastewater streams over an extended period. These measurements would help design engineers to select suitable systems for the separation of NC fines from the RAAP wastewater streams. Turbidity, zeta potential (particle surface charge), conductivity, and pH were also measured and analyzed. The amounts of NC lost to the settling pits from each purification process were calculated from the measured TSS concentrations and flow estimations from a previous study. The PSD, TSS, and mass balance results obtained in this study were compared to the results obtained in previous studies.

Gravity settling characteristics of mixed wastewater at poacher pits were determined. Settling tests were also performed with NC slurry from the poacher, blender, and wringer tubs to assess its settling characteristics in washing process.

Jar tests were conducted to assess the ability of a high charge cationic polymer to remove NC fines from the RAAP poacher pit wastewater by coagulation and flocculation. Additional jar tests were conducted to evaluate whether NC fine removal by coagulation and flocculation could be achieved by simple pH adjustment at acid boiling tub pits. Other useful information was obtained with the assistance of RAAP personnel and through past studies conducted on NC fines removal. Based on the characterization data and discussion with operators, a pollution prevention strategy was developed.

Scope

This study was to characterize NC fines in manufacturing process water and to provide basic NC fines physical characteristics information to be used for other NC fines separation and treatment projects. This report does not include information on chemical characterization of NC. This report developed pollution prevention ideas. Additional work may be needed to implement the ideas.

Mode of Technology Transfer

The information derived from this study will be used to provide statistically significant NC fines characteristic data to other 6.2 projects that will evaluate and develop NC fines separation and treatment technologies. It is recommended that the pollution prevention strategies devised in this work be validated through the Environmental Security Technology Certification Program (ESTCP) or Strategic Environmental Research and Development Program (SERDP) for use as guidelines for implementation/demonstration of NC fines pollution prevention.

Metric Conversion Factors

The following metric conversion factors are provided for standard units of measure used throughout this report:

1 in.	=	25.4 mm
1 ft	=	0.305 m
1 lb	=	0.453 kg
1 gal	=	3.78 L

2 Overview of Nitrocellulose Processes at RAAP

Overview of the Nitrocellulose Production Process

Figure 1 shows the NC production and wastewater flow schemes at the RAAP plant. The raw cotton or pulp NC passes through six unit operations:

1. The nitrator
2. The boiling tub house
3. The beater house
4. The poacher house
5. The blender house
6. The wringer house.

In the nitration step, cotton linter or wood pulp cellulose is nitrated using nitric and sulfuric acids. After nitration, most of the residual acid is removed from the NC using a counter-current backwash centrifuge. After the nitration phase, it is necessary to remove the remaining residual acid and stabilize the NC. This purification and stabilization is accomplished in the following steps:

1. The crude NC is repeatedly boiled over several days in the boiling tub house to remove most of the residual acid from the NC.
2. The NC is then cut and beaten in a slightly alkaline water in the beater house so as to reduce the average NC particle size and to reduce the remaining acid content.
3. The NC is next stabilized in the poacher house by boiling the NC with soda ash.
4. Then the NC is screened and vacuum filtered to remove the bulk water.
5. Various NC batches are combined in the blender house to achieve the desired final grade.
6. The NC is sent to the wringer house where it is centrifuged to remove excess water.

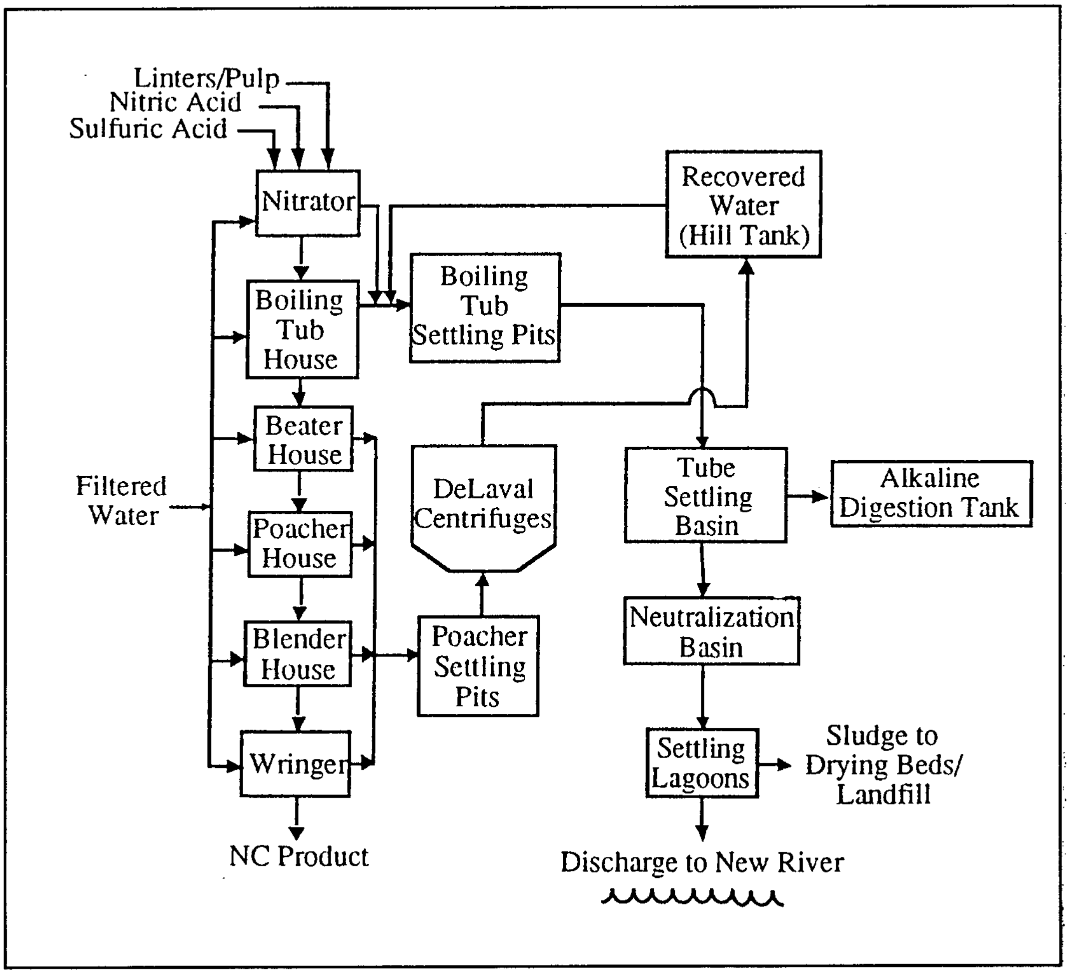


Figure 1. NC manufacturing and wastewater flow diagram.

These NC purification processes use filtered river water as wash and transfer water. After being dewatered in the wringer house, the NC is drummed and transported for further processing into propellant.

Overview of the NC Wastewater Treatment Process

All of the processes listed above discharge wastewater containing NC fines. Figure 1 also shows a schematic of the wastewater flow. Low pH wastewaters from the nitrator and boiling tub house drain to the boiling tub settling pits. The NC particles in the boiling tub house wastewater are generally larger than those in the wastewater from the four remaining processes because the NC is still uncut. Neutral or slightly alkaline pH wastewaters from the beater, poacher, blender, and wringer houses all drain to the poacher settling pits. These wastewaters contain a mixture of short NC fibers and colloidal fines that are generated during the beating operation. The effluent from the poacher settling pits is pumped through DeLaval centrifuges to remove nonsettleable NC fines. This reportedly reduces the suspended solids concentration to approximately 30 to 70 mg/L (Dehart and Musser

1993), although in this study, the centrifuge centrate TSS concentrations ranged from 4 to 17 mg/L. The backflush water from the DeLaval centrifuges containing the recovered NC is discharged back into the top poacher pits. The centrifuge centrate is pumped to the recovered water tanks (or hill tanks). The original plant designer's intent was to use the centrate as boiling tub makeup water and, at the same time, to neutralize acid boiling tub pit wastewater with this slightly alkaline water. In fact, the centrate was once used as process water in the boiling tub house; however, the effluent from the hill tanks now flows directly to the boiling tub settling pits. A major problem with using the recovered water tanks was accumulation of NC fines and fibers at the bottom of the tanks. Theoretically the centrate is very clean. However, accumulation of NC is practically inevitable. Although a substantial portion of the NC in the hill top tank might have accumulated before the centrifuge was built, it is evident that still a large quantity of NC is carried to the hill top tank when the tank is flushed. It is still an unresolved problem how to remove the accumulated NC at the bottom of the recovered water tanks without upsetting the boiling tub pit operation.

The effluent from the boiling tub settling pits is currently pumped directly to the neutralization basins where lime is added to raise the pH. The effluent from the neutralization basins flows to a final settling lagoon where additional NC fines and the calcium sulfate formed during neutralization are allowed to settle. A new final settling lagoon is being constructed to replace the existing settling lagoon. The final settling lagoon effluent discharges to the New River. Sludge from the settling lagoons is periodically removed, dried, and then landfilled on site.

A tube-settling/flow-equalization basin before the neutralization basins will be placed into service in the near future. This basin served as an equalization basin in the past and was recently being retrofitted for tube settling. The tube-settling basin will be periodically drained and the NC fines settled on the bottom will be pumped to a caustic digestion tank. The digested NC can be either transported off the plant for final disposal, or neutralized and pumped to the existing rotating biological contractors for biological treatment.

Overview of NC Recycling From Settling Pits

The NC that settles in the boiling tub settling pits (called "pit cotton") is periodically pumped back to boiling tub house to be reprocessed. Similarly, the NC that settles in the poacher pits (also called "pit cotton") can be pumped back to the poacher house and reprocessed. Figure 2 shows the pumping involved with recycling NC

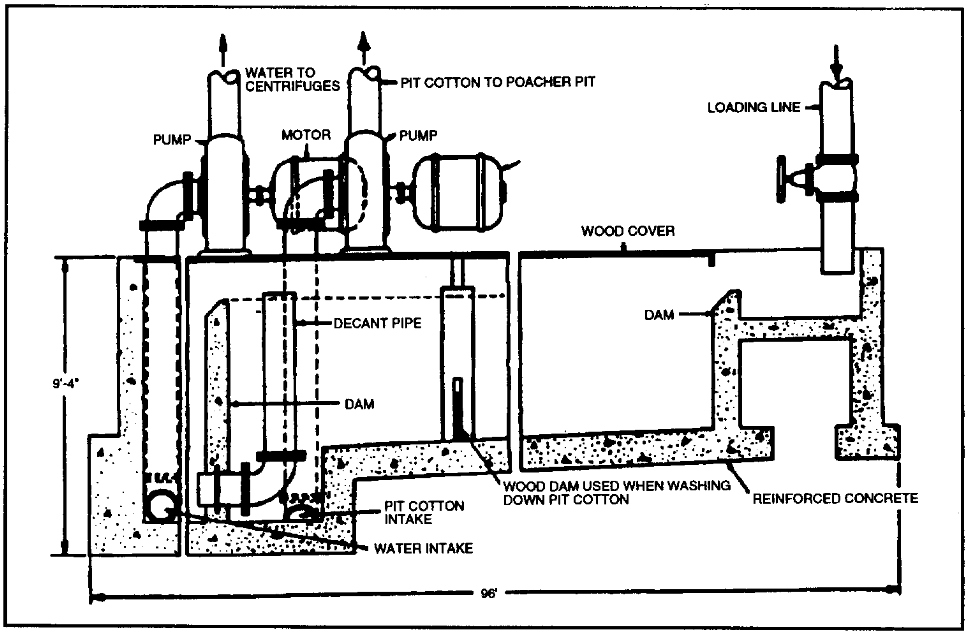


Figure 2. Blender and poacher settling pit.

from the poacher pits. The recovered pit cotton NC is only incorporated into low-grade propellant.

Various studies have been conducted to investigate options for removing and recovering fines from the NC manufacturing wastewaters. A study conducted by A.D. Little, Inc., identified cross-flow microfiltration as the most promising alternative (Balasco et al. 1987). This technology differs from conventional dead-ended filtration (e.g., reverse osmosis or ultrafiltration) in that the buildup of a static solids layer on the membrane is prevented by continually sweeping the feed wastewater over the surface. Subsequent pilot-scale studies demonstrated that larger NC particles (>100 µm) obstructed the filtrate flow through the microfiltration membranes, but that rotating vacuum filtration units could remove these larger particles upstream of the microfiltration units. It was consequently concluded that microfiltration preceded by a suitable prefiltration process could be an effective combination for removing and recycling fines in the NC wastewater (Kim et al. 1996). Additional studies are being conducted to further evaluate the potential of microfiltration for removing and recycling NC fines from the various process wastewater streams (Kim, Clark, and Lee 1997).

3 Unit Operations of NC Manufacture and Purification

Note that much of the information in this Chapter was taken from the RAAP NC production area operators training manual.

Nitrator

The process used to manufacture NC involves the nitration of cotton linters or wood pulp cellulose using a combination of nitric and sulfuric acids. During this nitration process, hydroxyl groups on the cellulose molecules are substituted with nitro-groups. After nitration, most of the residual acid is removed from the NC using a counter-current backwash centrifuge. Low pH wastewater is discharged to the boiling tub settling pits.

Boiling Tub House

Purification of the NC starts at the boiling tub house (see Figure 1). Each boiling tub (Figure 3) is initially filled with approximately 2 ft of filtered water. Then NC from the nitrator is transferred to the boiling tub by placing the loading hose in the tub door opening. The drain to the settling pit is opened when the tub is filled from 1/2 to 3/4 full. NC is continuously added until the tub is full, after which the acidity is checked. If the acidity meets the criteria, the NC is washed with filtered water to reduce the acidity. The wash water is then drained to the acid settling pits. After this wash cycle, the drain to the settling pits is closed and the NC is left covered with water.

After the boiling tub is loaded and any required washing is completed, an acid boil cycle is initiated. The drain is opened and the water level in the tub is dropped to 3 ft below the NC surface. Then the drain is closed and the perk system is started. The injected steam raises the temperature in the tub to approximately 98 °C and recycles the water through the NC. The acidity is checked routinely during the acid boil cycle. The acid boil is completed after 15 to 85 hours; different acid boil cycle times affect the viscosity of the NC product. After the acid boil is completed, the NC

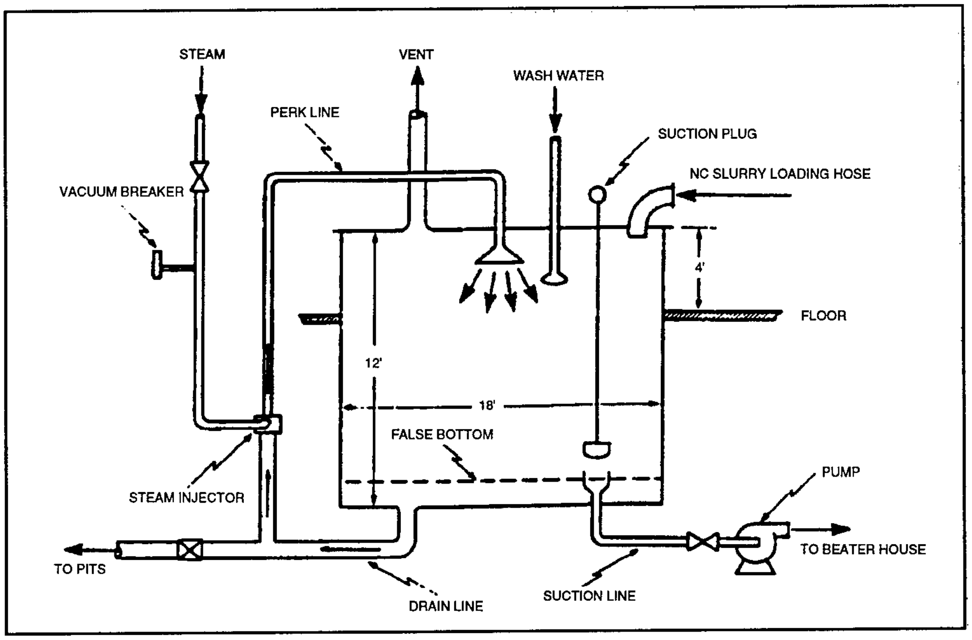


Figure 3. Boiling tub.

is again washed with filtered water, placed on a 5-hour neutral boil, followed by a second wash, another 5-hour neutral boil, and a third wash. The procedure for the neutral boils is the same as for the acid boil. The water from the wash cycles is again drained to the acid settling pits.

The plant operators believe that most of the NC that is discharged to the boiling tub settling pits probably escapes through the orifices in the boiling tub's false bottom during the initial few minutes after opening the drain. It is thought that a cake of NC eventually forms at each orifice, preventing further NC discharge to the settling pits.

When the boiling and washing treatment cycle is completed, the NC is pumped to the beater house. A fire hose is used to wash the NC mass into the suction line. Since this method creates more NC slurry than can be held in the beater house receiving tubs (T-1 and T-2), it is necessary to send the slurry in intervals called "shots." Before and after each shot, operators flush the slurry lines with water to prevent NC from settling out of the slurry and plugging the line.

Beater House

When a beater house receiving tub (T-1 or T-2) is partially full, the tub agitators are started (Figure 4). As the tub continues to fill, soda ash is added until the NC slurry has been neutralized.

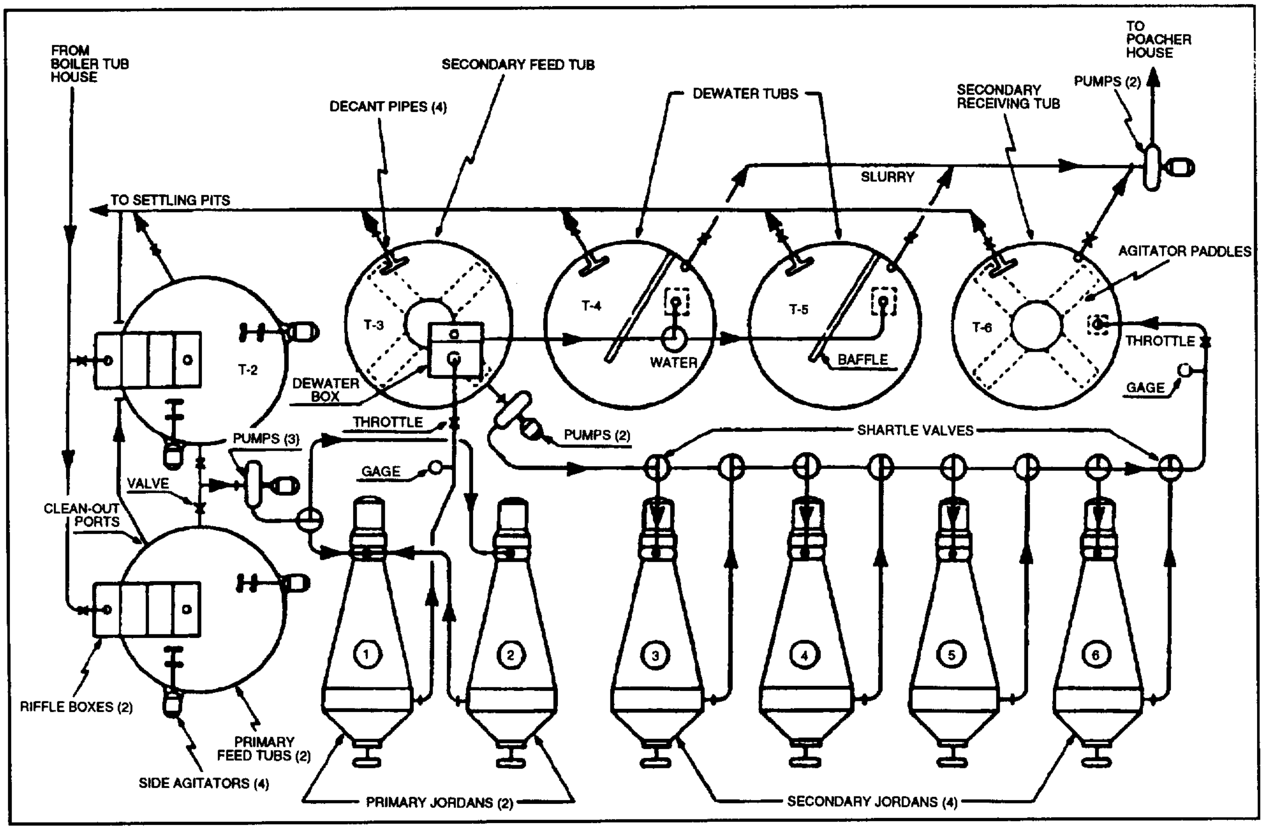


Figure 4. Beater house plan.

When the receiving tubs are sufficiently full, the primary beaters are started and the slurry is simultaneously cut as it is received. Once the NC level in the receiving tub reaches 10 ft, the pumping of slurry is stopped; when the slurry level drops to 3 to 4 ft above the bottom, pumping of slurry is again resumed. Slurry from the primary beaters is pumped to the dewater box on top of the secondary feed tub T-3 (Figure 5). Here the NC slurry flows over a sloped screen, allowing part of the slurry water to be diverted to the dewater tubs (T-4 and T-5). The proper slurry consistency must be attained in tub T-3 if the secondary beaters are to function properly. A return line and valve may be used to return improperly cut material from the secondary feed tub to the primary tubs.

Once the slurry reaches a desirable consistency in tub T-3, operators start slurry flow to the secondary beaters. The operators set the power level and back pressure on each beater as determined from previous cuttings. The fine cut slurry enters the secondary receiving tub T-6. When the amount of NC cut equals the capacity of a poacher tub (approximately 10,000 lb of pulp or 12,000 lb of cotton), the slurry in tub T-6 is pumped to the poacher house.

When a dewater tub (T-4 or T-5) is full, the operator lowers a decant pipe (fitted with a perforated head with approximately 1/16 in. diameter holes) into the supernatant,

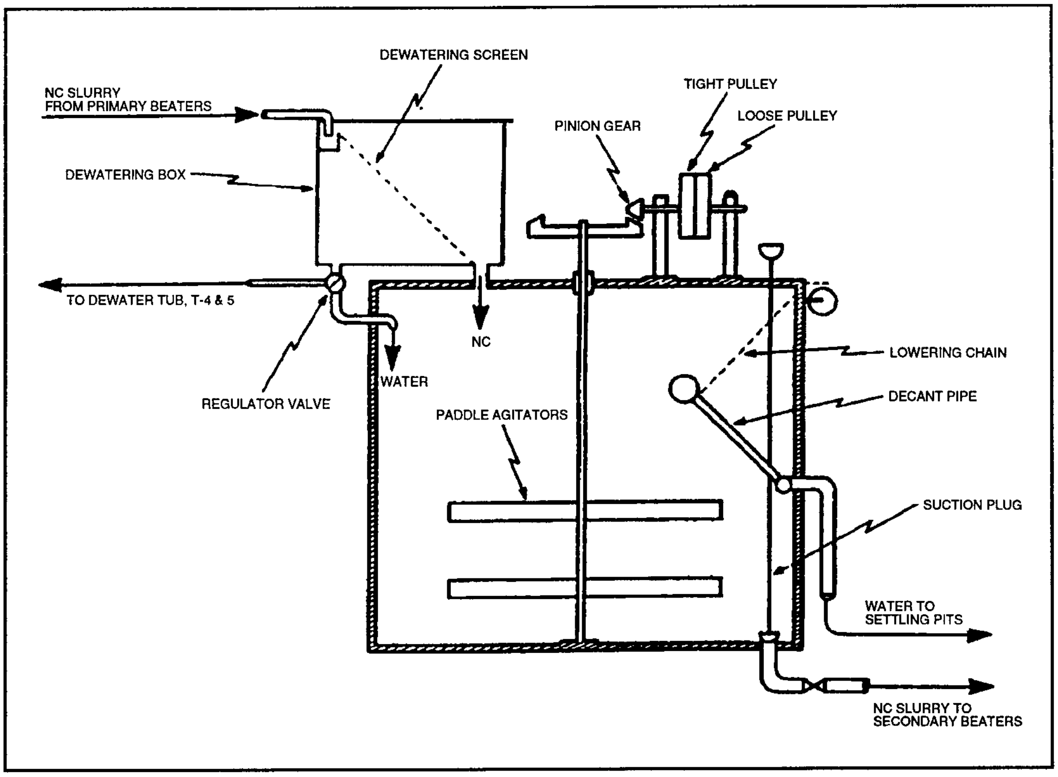


Figure 5. Secondary feed tub, T-3.

which then flows by gravity to the poacher settling pits. The remaining NC slurry in the dewater tub (6 to 8 in.) is then pumped to the poacher house.

To prevent contamination, all equipment and piping are thoroughly cleaned between processing of different types of NC. The pipe lines and pumps are completely flushed with water before and after use, and the beaters are flushed thoroughly at each shut-down.

Poacher House

Figure 6 shows a schematic of a single poacher tub. When a poacher tub is ready to start the poaching cycle, approximately 3 ft of water is decanted from the tub, and the steam injection boil cycle is started. The NC receives a 4-hour soda boil (where soda ash is added), followed by a 2-hour neutral boil, and two 1-hour neutral boils. After each of the first three boil cycles, about 3 ft of filtered water is added and the NC is subjected to an agitated wash. After each wash, the NC is allowed to settle, approximately 4 ft of the supernatant is decanted, and the next boil cycle is started. All the decanted water flows to the poacher pits. A listing of the poaching treatment process appears in Table 1.

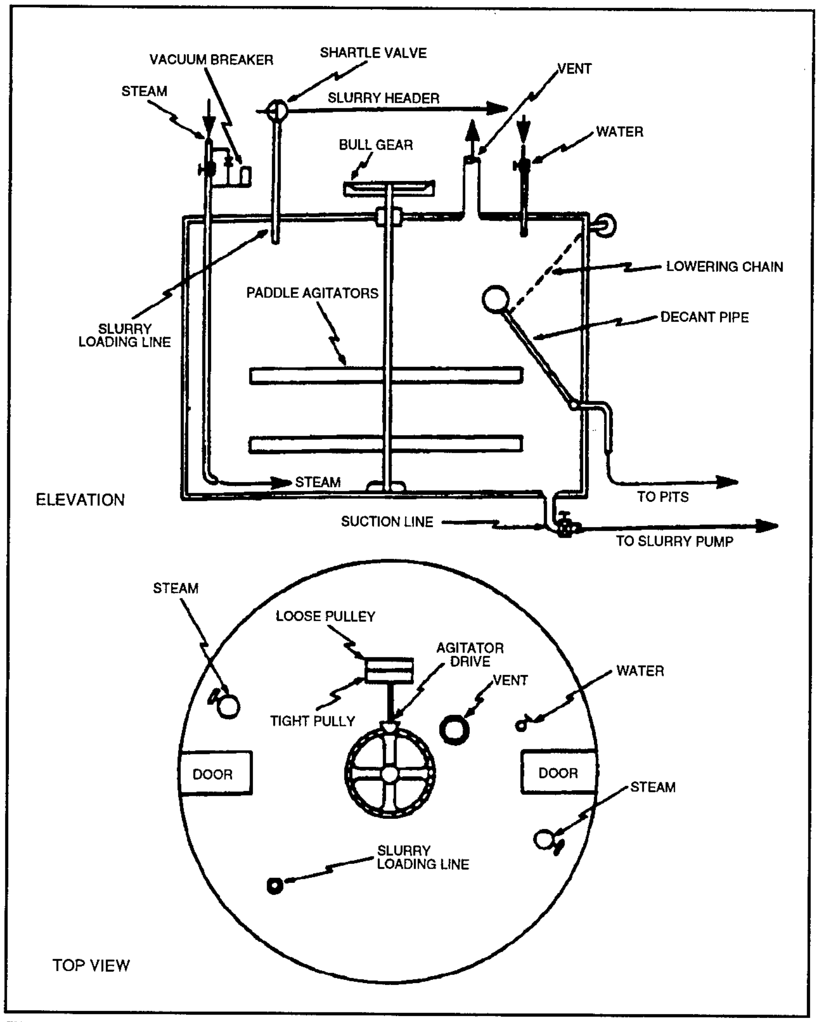


Figure 6. Poacher tub.

Table 1. Poacher treatment requirements for all types of NC and pit cotton.

	Soda Ash	Boiling Temp.	Boiling Time	Agitated Wash	Settling Times*		Drain
Soda boil	4 lb/ 1000	96 C	4 hr	15 min.	60 min.	30 min.	45"
Neutral boil	none	96 C	2 hr	15 min.	60 min.	30 min.	45"
Neutral boil	none	96 C	1 hr	15 min.	60 min.	30 min.	45"
Neutral boil	none	96 C	1 hr	none	not required		none

*Settling times may be increased or decreased at discretion of operators.

After the poaching cycle is complete, the NC slurry is pumped across a vibrating screen to remove any large uncut fibers (Figure 7). The larger NC particles collected on the screen are returned to the beater house to be recut. The NC slurry that passes through the vibrating screen flows down a riffle box where additional high density particles are removed, across a magnet where any metal particles are removed, and into the filter feed tub. The NC slurry is then pumped to a rotary vacuum filter with a fixed metal screen to be washed and dewatered. The filtrate from this process flows to the tail water tub, from where it then flows to the poacher settling pits. The dewatered NC slurry is mechanically scraped from the vacuum filter drums and stored in storage tubs below. The dewatered NC is then pumped to tubs in the blender house.

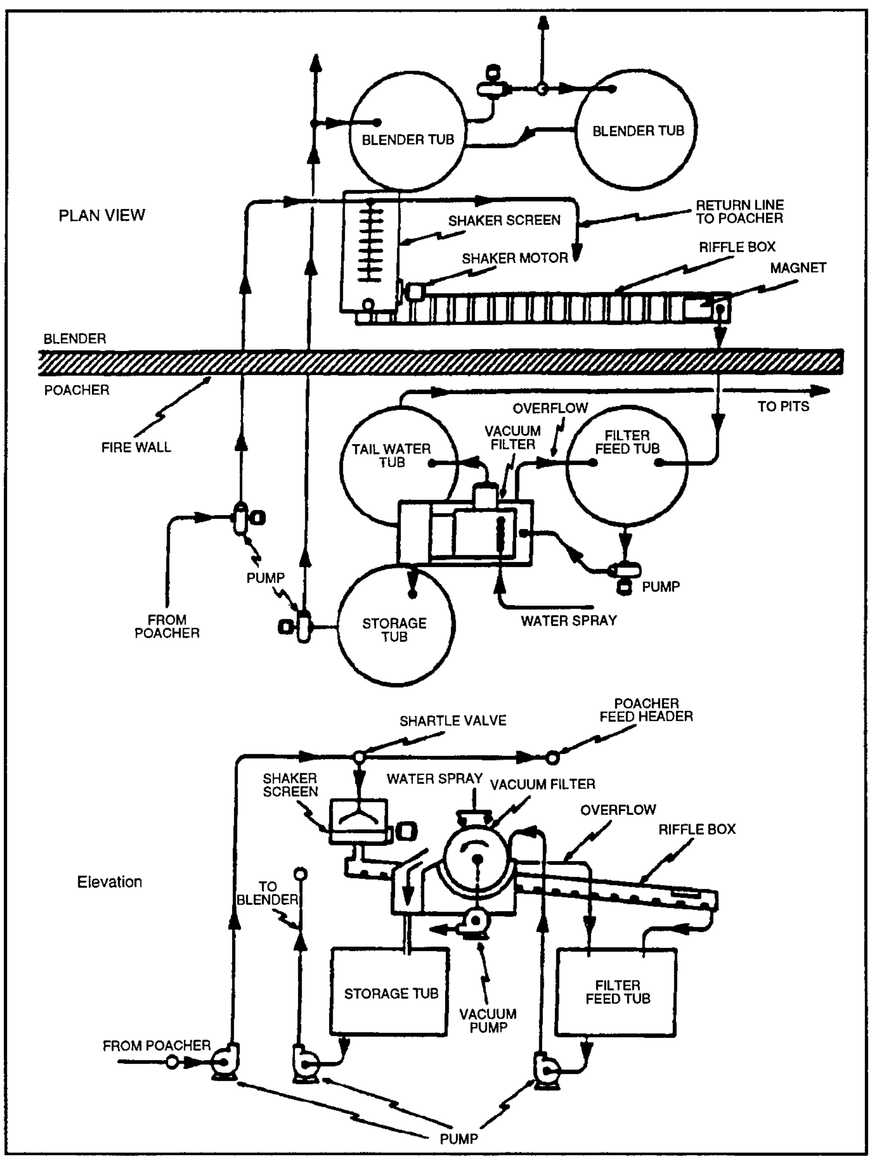


Figure 7. Slurry filler process flow.

Blender House

At the blender house, different types of NC are blended together to achieve the required nitrogen contents and properties. A typical blend is 22,000 lb. Two tubs each containing 11,000 lb of NC are used (Figure 8). The blend is agitated for 6 hours. Then the NC fibers are allowed to settle and approximately 2 ft of water is decanted off of each tub. The NC is then transferred to the wringer house by using a fire hose to flush the NC out of the tubs. Note that there is considerable variability in the water use rate for the blending processes because different NC blends require different numbers of transfers from the poacher tubs to the blender tubs and thus also different numbers of line and tub washes.

Wringer House

After receiving a transfer of NC slurry from the blender house, the slurry is allowed to settle for at least 1 hour in the wringer house receiving tubs (Figure 9). Then the water above the NC blend is decanted off, leaving 18 in. The agitator and circulating pump are started to agitate the slurry and pump it through the circulating line back to the tub, ensuring a consistent mixture of NC and water.

After initiating the agitator and circulating pumps, the wringing operation is started. With the wringer basket revolving at low speed, the shartle valve on the circulating line is opened and the basket is allowed to fill through a perforated loading pipe (Figure 10).

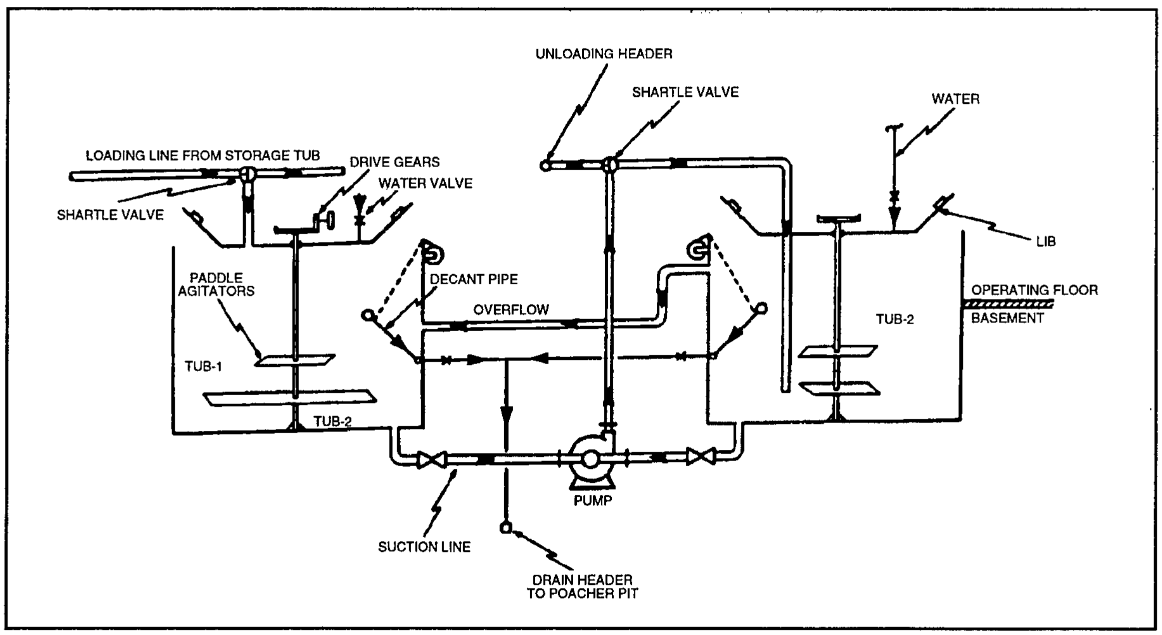


Figure 8. Blender arrangement.

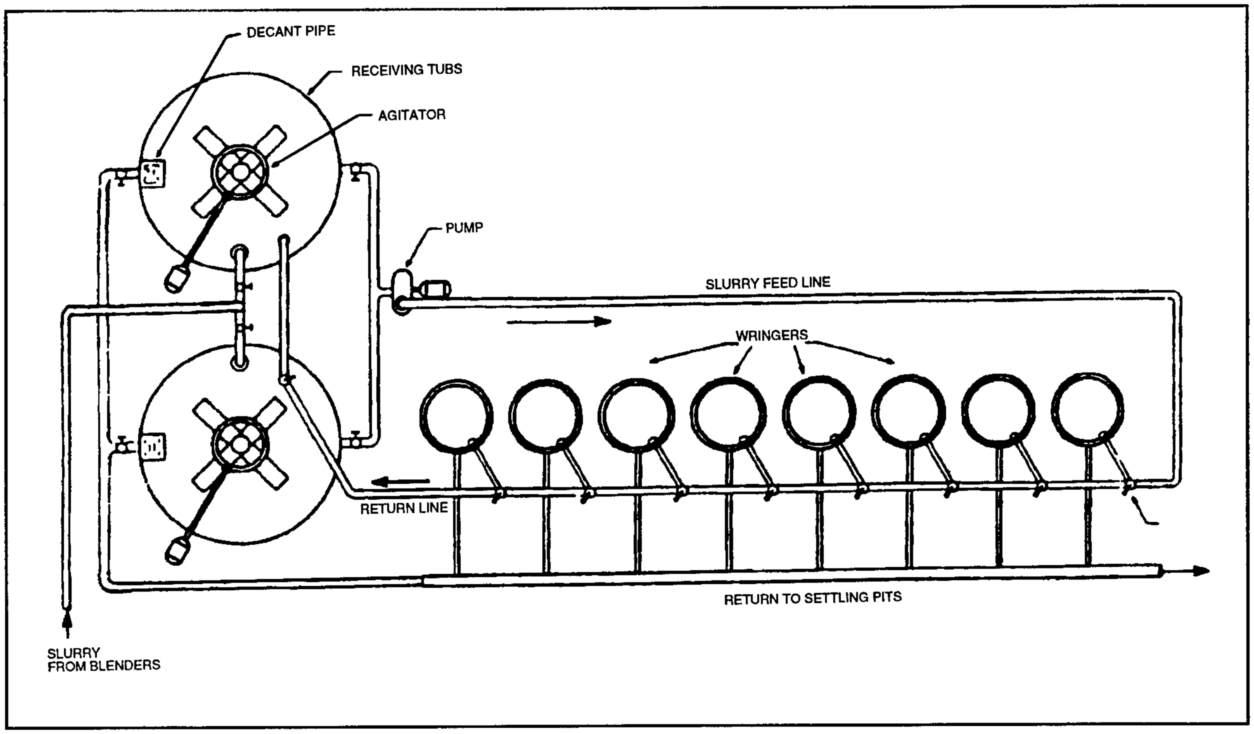


Figure 9. Final wringer.

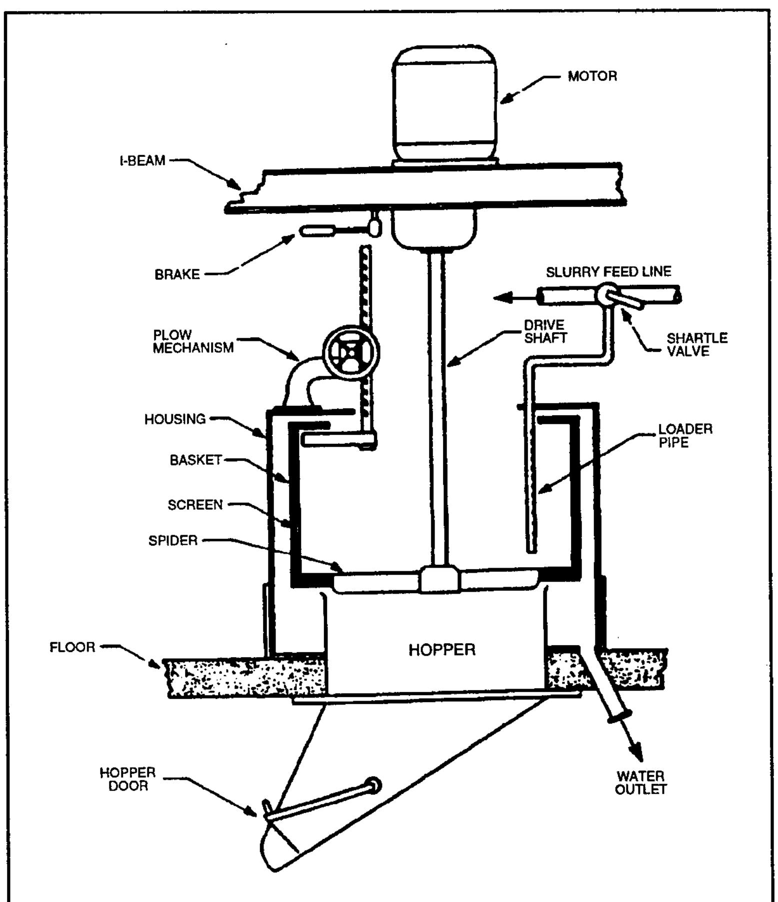


Figure 10. Centrifugal wringer.

The centrifugal force generated by the revolving basket causes the NC to cake up on the vertical sides of the basket. When the cake has built up sufficiently to touch the preset loader gauge, the shartle valve on the circulating line is closed and the basket is revolved at high speed to dewater the NC.

After a set period of time, the wringer rotation is stopped by applying the brake. The NC cake is then removed from the basket using the attached plow mechanism. With the basket rotating slowly, the plow is slowly pulled forward and the NC cake is plowed from top to bottom. This removes most of the cake, which falls through the spider bottom of the basket into a hopper. A thin layer of NC cake is left on the basket screen to prevent the loss of NC fibers through the screen during the following wringing cycles.

After the wringing operation, the NC in the hopper is transferred to empty cans and weighed. The loaded cans are then pushed onto the revolving monorail and transported to the dehydration part of the plant.

4 Sampling and Analytical Methods

NC Wastewater Sampling

The sampling of the various NC production wastewater streams occurred during two separate periods due to NC production being switched over from the A-B-line to the C-line when the sampling was first started. Consequently, the beater house, poacher house, blender house, wringer house, poacher settling pit, DeLaval centrifuge centrate, and recovered water tank samples were collected while NC was being processed on the A-B-line, while the boiling tub house, boiling tub settling pit, basin 3054, neutralization basin, and final settling lagoon samples were collected while NC was being processed on the C-line. Figures 11 and 12 show the NC product and wastewater flow schemes during the first and second sampling periods. Note that the NC fine concentrations in samples collected from all the wastewater treatment facilities (boiling tub settling pit, poacher settling pit, DeLaval centrifuge centrate, recovered water tank, neutralization basin, and final settling lagoon) were probably lower than normal as a result of the switch-over in production lines. However, the samples collected from the NC production wastewaters (boiling tub house, beater house, poacher house, blender house, and wringer house) should have been representative of normal conditions.

Wastewater samples (500 mL) were collected from the following locations during the two sampling periods:

1. Boiling tub discharge line to settling pits (during initial loading and during each of the three wash cycles)
2. Beater house dewater tub supernatant
3. Poacher house tub supernatant (after each of the first three boil cycles)
4. Poacher house vacuum drum filter tail water
5. Blender house tub supernatant
6. Wringer house tub supernatant
7. Wringer house centrate (during clean screen load, wringing cycle, and caked screen load)
8. Boiling tub settling pit (inlet and outlet)
9. Basin 3054 (inlet)
10. Poacher settling pit (inlet and outlet)

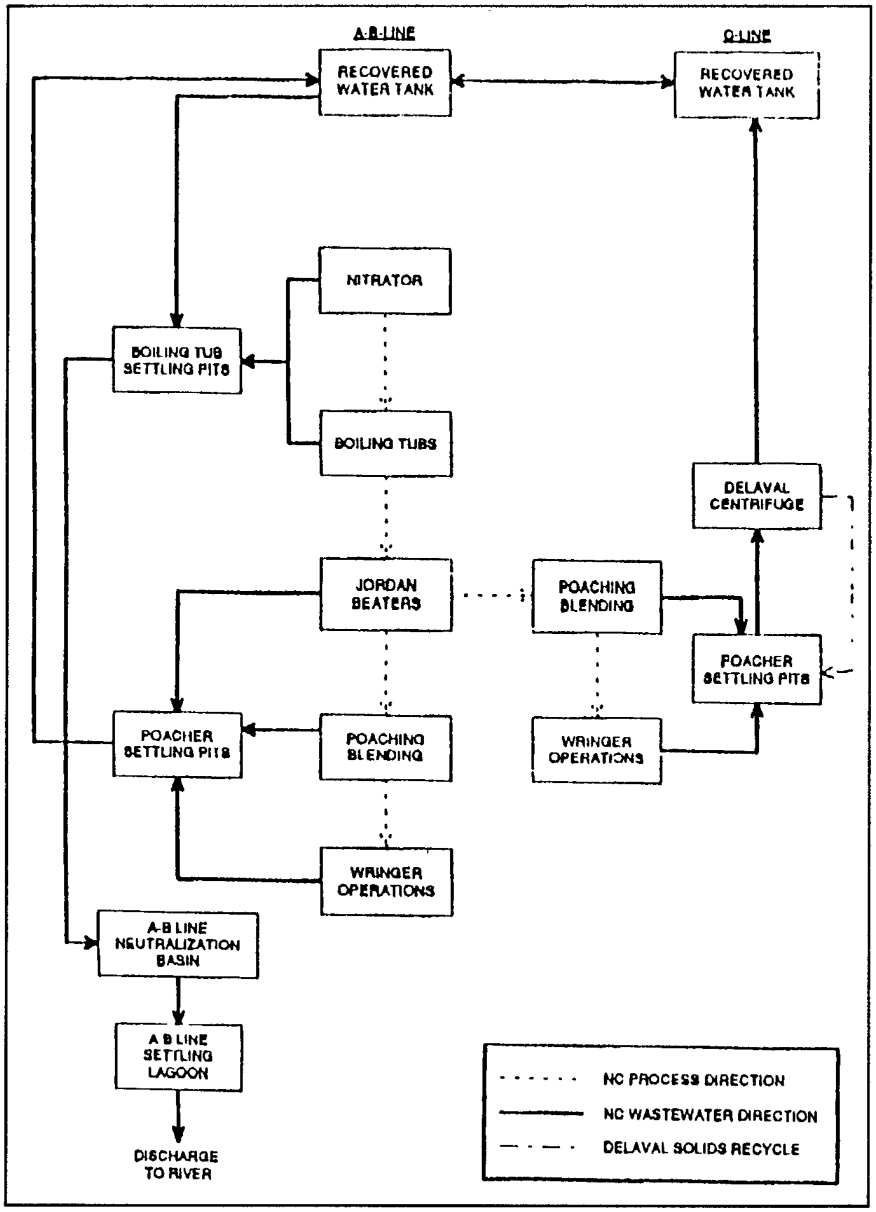


Figure 11. Final schematic for first sampling period.

11. DeLaval centrifuge centrate
12. Recovered water tank effluent
13. Neutralization basin (influent and effluent)
14. Settling lagoon (influent and effluent).

Wastewater samples were taken for both pulp and cotton NC batches. These wastewater samples were analyzed for PSD, turbidity, conductivity, and pH, and then saved and later shipped to the UW for zeta potential and TSS analyses. In addition, 1 L cotton and pulp slurry samples (NC mixed with water) were collected from all the tubs that decanted wastewater to the settling pits so that settling tests could be performed. Finally, a 5-gal wastewater sample was collected from the

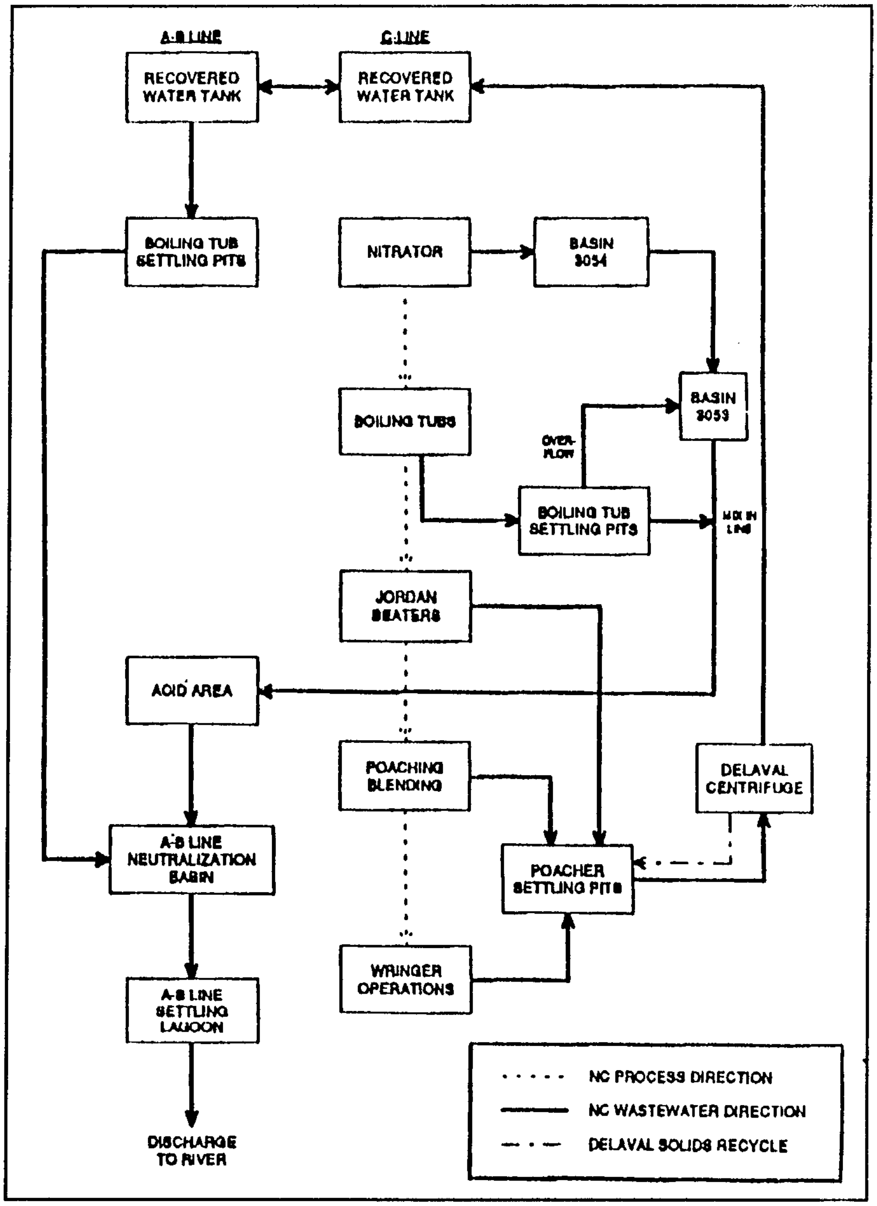


Figure 12. Final schematic for second sampling period.

poacher pit inlet so that jar tests using polymer could be done. Another 5-gal sample was later collected from the poacher pit inlet and shipped to the UW so that jar tests could be performed in which only pH was adjusted.

NC Wastewater Characterization

The particle size distribution tests were performed using a Brinkmann Particle Size Analyzer (PSA). This test involves placing 2 mL of sample in a small plastic cuvette and then placing the cuvette between a laser source and a detector. A small magnetic stir bar mixes the sample. The PSA measures the size of particles by

detecting the length of time that the particles interfere with the path of the laser. Thousands of measurements are made in a few minutes. A computer program then compiles the data and lists the particle size distribution *based on percentage of the cumulative particle volume assuming all particles are spherical.* The assumption of spherical particles is not strictly applicable since NC fines are irregularly shaped. However, the PSA test should still provide a good indication of the relative distribution of the particle sizes.

After performing the particle size analyses, the samples were tested for turbidity, conductivity, and pH. The turbidity analyses were conducted with an electronic turbidimeter calibrated with 0.9, 9, 90, and 900 Nephelometric Turbidity Units (NTU) standards (note that turbidity measurements of above 1000 NTU are therefore cited as ">1000 NTU"). The conductivity and pH measurements were made with calibrated conductivity and pH meters. The samples were then shipped to the UW, where TSS analyses were conducted using 0.8 μm pore size filters as per RAAP temporary procedure #L-38.

The surface chemistry of the NC particles in the RAAP wastewater samples were analyzed at UW with a Pen Kem, Inc. System 3000. This measures the velocities of the particles that result from the application of an electric field. This measurement is called the electrophoretic mobility. The electric field is created by two electrodes with a known voltage difference. The particle velocities are then measured by laser and sensor. The average particle zeta potential (or surface charge) is in general linearly proportional to the electrophoretic mobility, i.e., zeta potential (mV) = constant x electrophoretic mobility (m^2/V-sec).

Jar Tests

The jar tests were conducted with a standard jar test apparatus. The first set of jar tests were conducted at the RAAP plant to assess the ability of polymer to remove turbidity from the poacher pit wastewater by coagulation and flocculation. Rhone-Poulenc* Clarifloc cationic C-4450 polymer was selected based on performance comparison with a few polymers. It was a high charge cationic polymer made of acrylamide copolymers and cationic monomers. Approximately 14 L of sample were collected from the inlet end of the poacher pit. Small volumes of the concentrated polymer solution were added to six plastic jars, each containing 2 L of the poacher pit wastewater to achieve polymer concentrations of 0.1, 0.5, 1.0, 5.0, 7.5, and 10.0 mg/L, respectively. The polymer solution was rapidly added to each jar at a mixing

* Parsippany, NJ, telephone number 800-848-POLY.

speed of 100 rpm for a few seconds and then immediately reduced to 75 rpm for 15 minutes, followed by 50 rpm for 7.5 minutes, 25 rpm for 75 minutes, and then 30 minutes of quiescent settling. During the settling period, aliquots were withdrawn from the top 200 mL of each jar every 5 minutes and tested for turbidity. At the end of the test, the final pHs were measured.

A previous study found that the iso-electric point (the pH at which the surface charge of colloidal particles is neutralized) for the poacher pit wastewater to be approximately 1.9 (UW study, Peng et al. 1992). It was thus hypothesized that reducing the pH of the poacher pit wastewater would reduce the repulsive force between particles, thus ultimately leading to the flocculation and settling of the NC fines. A second set of jar tests were conducted at the UW to test this hypothesis. Another 14 L sample was collected from the poacher pit influent and shipped to the UW. Seven 2 L plastic jars were filled with the wastewater sample and adjusted to pHs of 1.6, 2.5, 4.0, 5.5, 7.0, 9.0, and 10.5, respectively, using sulfuric acid or sodium hydroxide. The jar tests were then conducted as described in the preceding paragraph.

The pH adjusted jar tests described above did not show the expected decrease in turbidity at the low pH values. Consequently, the pH adjustment jar tests were repeated using left over poacher pit wastewater that had previously been shipped to the UW for laboratory microfiltration tests. Eleven different pH levels were employed during these second pH adjustment jar tests: 2.0, 2.5, 4.0, 5.0, 7.0, 9.0, 10.0, 10.5, 11.0, 11.5, and 11.8. These tests were also conducted as described above.

Slurry Settling Tests

The initial zone-settling velocities of the NC slurry samples were determined by pouring the slurry into 1 L graduated cylinders and measuring the height of the solids/liquid interface over time.

5 Experimental Results

NC Wastewater Characterization

Tables 2 through 6 show the PSD, TSS, and turbidity results for the NC purification wastewaters, while Tables 7 through 11 show the zeta potential, conductivity, and pH results. The values shown are averages of three or more replicate analyses, except for TSS, for which only one analysis was performed per sample.

Note that, although the Brinkmann PSA used in this study provided quick and inexpensive PSD measurements, there are some potential problems with the PSA generated results. First, the PSD measurements (percentages of particles in a given size range) obtained using the PSA were the percentages of the total cumulative *volume* of particles in the analyzed samples, *assuming all particles to be spherical* (see Chapter 4). Previous studies using filtration methods have obtained PSD results based on the percentage of cumulative *mass*, which would be the more pertinent measurement (although the PSD results based on volume should correlate roughly with PSD results based on mass, assuming the specific gravity of the NC particles is roughly the same for different particle volumes). In addition, the assumption of spherical particles is not strictly applicable for NC particles since the NC fines are irregularly shaped. Since no tests were performed with NC wastewater to explicitly compare PSD results using the PSA and filtration methods, the significance of the differences above is not known. Secondly, the PSA method employs aliquots of only 2 mL for analysis (see Chapter 4), which resulted in significant variability between replicate analyses (e.g., the difference of a few large particles lead to drastically different PSD results in samples with low suspended solids concentrations). While at least three PSD tests were conducted for each sample, no statistical analyses were performed to evaluate the variability between the replicate trials.

Despite the problems discussed above, it is believed that the PSD results obtained in this study using the Brinkmann PSA should still provide a relative indication of the distribution of NC particle sizes in the various NC production wastewater streams. The PSD analyses showed that the NC fines in the various tub supernatant samples were predominantly below 10 µm.

Table 2. PSD, TSS, and turbidity results for pulp NC processing wastewaters.

Sampling Location		Percent by volume in indicated range (microns)								TSS mg/L	Turb. NTU
		1-10	10-20	20-30	30-40	40-60	60-80	80-100	>100		
Boil. tub during load-	after 0 min	na	na	na	na	na	na	na	na	26	8
	after 5 min	na	na	na	na	na	na	na	na	16	1
	after 30 min	na	na	na	na	na	na	na	na	2	0
Boil. tub 20 hr after boil	after 0 min	na	na	na	na	na	na	na	na	2	1
	after 5 min	na	na	na	na	na	na	na	na	4	1
	after 30 min	na	na	na	na	na	na	na	na	2	1
Boil. tub after 1st 5 hr boil	after 0 min	na	na	na	na	na	na	na	na	10	6
	after 5 min	na	na	na	na	na	na	na	na	6	1
	after 30 min	na	na	na	na	na	na	na	na	10	1
Boil. tub after 2nd 5 hr boil	after 0 min	na	na	na	na	na	na	na	na	32	5
	after 5 min	na	na	na	na	na	na	na	na	6	3
	after 30 min	na	na	na	na	na	na	na	na	1	1
Beater super. settled 1 hr		81	2	5	13	0	0	0	0	118	75
Poach. super. settled 1 hr after 1 boil		81	0	10	10	0	0	0	0	139	>1000
Poach. super. settled 1 hr after 3 boil		86	10	4	0	0	0	0	0	183	>1000
Blender vac. drum tail water		54	4	2	3	7	3	0	28	290	>1000
Blender super. settled 1 hr		99	1	0	0	0	0	0	0	433	>1000
Wringer super. settled 1 hr		100	0	0	0	0	0	0	0	286	>1000
Wringer super. settled 24 hr		93	4	0	0	3	0	0	0	112	>1000
Wringer centrate, clean screen load		18	10	15	7	15	15	3	17	385	333
Wringer centrate, caked screen load		13	6	9	12	35	14	2	10	40	12

However, the PSD results for the vacuum drum tail water, wringer filtrate, and poacher settling pit inlet and outlet samples were distributed over a range of zero to >100 µm. The larger particle sizes in the vacuum drum tail water and wringer filtrate samples can probably be attributed to these wastewater streams not being settled to remove solids before being discharged to the poacher pits. The larger particle sizes in the poacher settling pit samples can probably be attributed to the poacher pit receiving the vacuum drum tail water and wringer filtrate, and to the practice of discharging the DeLaval centrifuge backflush water back into the poacher pits. No reliable PSD results were obtained for the boiling tub, boiling tub settling pit, DeLaval centrifuge centrate, neutralization basin, or settling lagoon samples due to the low TSS concentrations.

The TSS concentrations in the boiling tub drain samples ranged from zero to 43 mg/L, while the TSS concentrations in the various tub supernatants were generally quite high, ranging from 108 to 601 mg/L. The cotton NC supernatants generally had higher TSS concentrations than the pulp NC supernatants. In addition, the TSS concentrations in the tub supernatants that had been allowed to settle for more than 1 day were significantly lower than in those that had been allowed to settle

Table 3. PSD, TSS, and turbidity results for cotton processing wastewaters.

Sampling Location		Percent by volume in indicated range (microns)								TSS mg/L	Turb. NTU
		1-10	10-20	20-30	30-40	40-60	60-80	80-100	>100		
Boil. tub during load	after 0 min	na	na	na	na	na	na	na	na	43	22
	after 5 min	na	na	na	na	na	na	na	na	28	9
	after 30 min	na	na	na	na	na	na	na	na	15	2
Boil. tub after 20 hr boil	after 0 min	na	na	na	na	na	na	na	na	13	2
	after 5 min	na	na	na	na	na	na	na	na	6	1
	after 30 min	na	na	na	na	na	na	na	na	4	1
Boil. tub after 1st 5 hr boil	after 0 min	na	na	na	na	na	na	na	na	13	1
	after 5 min	na	na	na	na	na	na	na	na	6	1
	after 30 min	na	na	na	na	na	na	na	na	4	0
Boil. tub after 2nd 5 hr boil	after 0 min	na	na	na	na	na	na	na	na	0	0
	after 5 min	na	na	na	na	na	na	na	na	0	0
	after 30 min	na	na	na	na	na	na	na	na	0	0
Beater super. settled 1 hr		23	8	24	7	21	10	7	0	108	592
Poach. super. settled 1 hr after 1 boil		100	0	0	0	0	0	0	0	602	>1000
Poach. super. settled 1 hr after 2 boil		97	3	0	0	0	0	0	0	438	>1000
Poach. super. settled 1 hr after 3 boil		98	2	0	0	0	0	0	0	340	>1000
Poach. super. settled 1 hr after 1 boil		100	0	0	0	0	0	0	0	589	>1000
Poach. super. settled 1 hr after 2 boil		91	6	2	0	0	0	0	0	565	>1000
Poach. super. settled 1 hr after 3 boil		97	0	0	0	0	3	0	0	408	>1000
Blender vac. drum tail water		11	10	18	26	20	7	3	6	77	47
Blender super. settled 1 hr		93	7	0	0	0	0	0	0	555	>1000
Blender super. settled 7 days		100	0	0	0	0	0	0	0	155	>1000
Wringer super. settled 1 hr		86	10	4	0	0	0	0	0	338	>1000
Wringer super. settled 13 days		90	1	3	0	5	0	0	0	81	105
Wringer centrate, clean screen load		22	10	19	18	19	13	0	0	3660	>1000
Wringer centrate, during wringing		42	9	9	11	8	8	9	3	120	470
Wringer centrate, caked screen load		8	10	28	18	21	6	5	4	27	15

only 1 hour may be attributable to the NC fines being kept in suspension by temperature gradient induced turbulence while the tubs are cooling; once the tubs are completely cooled, the supernatant may become more quiescent. The TSS in the poacher pit inlet samples ranged from 53 to 250 mg/L, while the outlet samples ranged from 107 to 171 mg/L.

The TSS concentrations in the DeLaval centrifuge centrate samples were lower than reported in previous studies, ranging from 4 to 17 mg/L. The TSS concentrations in the samples from the boiling tub settling pits, basin 3054, and the neutralization basin influent were generally below 10 mg/L. The TSS for the neutralization basin effluent samples were higher than for the influent samples (ranging from 6 to 62 mg/L), probably as a result of the formation of calcium sulfate and other precipitates due to the addition of lime. The TSS concentrations in the settling lagoon influent and effluent samples were consistently below 10 mg/L. Note that the final settling lagoons receive wastewater from sources besides the neutralization basin effluent.

Table 4. PSD, TSS, and turbidity results for Basin 3054 and Boiling tub settling pit.

Sampling Location	Percent by volume in indicated range (microns)								TSS mg/L	Turb. NTU
	1-10	10-20	20-30	30-40	40-60	60-80	80-100	>100		
Basin 3054 inlet 9/30	na	na	na	na	na	na	na	na	12	6
Basin 3054 inlet 10/1	na	na	na	na	na	na	na	na	4	2
Basin 3054 inlet 10/4	na	na	na	na	na	na	na	na	2	1
Basin 3054 inlet 10/5	na	na	na	na	na	na	na	na	8	4
Basin 3054 inlet 10/6	na	na	na	na	na	na	na	na	10	5
Boiling tub settling pit inlet 9/30	na	na	na	na	na	na	na	na	0	0
Boiling tub settling pit inlet 10/1	na	na	na	na	na	na	na	na	2	1
Boiling tub settling pit inlet 10/4	na	na	na	na	na	na	na	na	3	2
Boiling tub settling pit inlet 10/5	na	na	na	na	na	na	na	na	1	1
Boiling tub settling pit inlet 10/6	na	na	na	na	na	na	na	na	20	0
Boiling tub settling pit outlet 9/30	na	na	na	na	na	na	na	na	1	1
Boiling tub settling pit outlet 10/1	na	na	na	na	na	na	na	na	9	6
Boiling tub settling pit outlet 10/4	na	na	na	na	na	na	na	na	3	3
Boiling tub settling pit outlet 10/5	na	na	na	na	na	na	na	na	5	2
Boiling tub settling pit outlet 10/6	na	na	na	na	na	na	na	na	6	1

Table 5. PSD, TSS, and turbidity results for poacher settling pit, DeLaval centrifuge centrate, and recovered water tank effluent.

Sampling Location	Percent by volume in indicated range (microns)								TSS mg/L	Turb. NTU
	1-10	10-20	20-30	30-40	40-60	60-80	80-100	>100		
Poacher pit inlet 8/26	6	3	4	7	17	11	21	32	53	17
Poacher pit inlet 8/27	27	9	7	9	24	6	6	11	250	592
Poacher pit inlet 8/31	19	8	6	8	11	7	15	25	90	187
Poacher pit inlet 9/1	91	5	4	0	0	0	0	0	197	>1000
Poacher pit outlet 8/26	10	5	6	9	21	14	9	27	171	37
Poacher pit outlet 8/27	31	10	7	6	20	10	2	4	107	236
Poacher pit outlet 8/31	28	13	13	12	16	11	3	7	119	264
Poacher pit outlet 9/1	49	9	9	0	10	15	6	5	135	470
Centrifuge centrate 8/26	na	na	na	na	na	na	na	na	6	4
Centrifuge centrate 8/27	na	na	na	na	na	na	na	na	7	8
Centrifuge centrate 8/31	na	na	na	na	na	na	na	na	17	13
Centrifuge centrate 9/1	na	na	na	na	na	na	na	na	4	7
Recovered water tank effluent 8/26	na	na	na	na	na	na	na	na	3	3
Recovered water tank effluent 8/27	na	na	na	na	na	na	na	na	13	4
Recovered water tank effluent 8/31	na	na	na	na	na	na	na	na	9	5
Recovered water tank effluent 9/1	na	na	na	na	na	na	na	na	4	5

Table 6. PSD, TSS, and turbidity results for neutralization basin and settling lagoon.

Sampling Location	Percent by volume in indicated range (microns)								TSS mg/L	Turb. NTU
	1-10	10-20	20-30	30-40	40-60	60-80	80-100	>100		
Neutralization basin inlet 9/30	na	na	na	na	na	na	na	na	8	11
Neutralization basin inlet 10/1	na	na	na	na	na	na	na	na	11	11
Neutralization basin inlet 10/4	na	na	na	na	na	na	na	na	2	4
Neutralization basin inlet 10/5	na	na	na	na	na	na	na	na	5	11
Neutralization basin inlet 10/6	na	na	na	na	na	na	na	na	13	16
Neutralization basin outlet 9/30	na	na	na	na	na	na	na	na	25	14
Neutralization basin outlet 10/1	na	na	na	na	na	na	na	na	62	25
Neutralization basin outlet 10/4	na	na	na	na	na	na	na	na	6	3
Neutralization basin outlet 10/5	na	na	na	na	na	na	na	na	14	17
Neutralization basin outlet 10/6	na	na	na	na	na	na	na	na	21	19
Settling lagoon inlet 9/30	na	na	na	na	na	na	na	na	3	3
Settling lagoon inlet 10/1	na	na	na	na	na	na	na	na	3	3
Settling lagoon inlet 10/4	na	na	na	na	na	na	na	na	2	4
Settling lagoon inlet 10/5	na	na	na	na	na	na	na	na	3	3
Settling lagoon inlet 10/6	na	na	na	na	na	na	na	na	5	3
Settling lagoon outlet 9/30	na	na	na	na	na	na	na	na	5	1
Settling lagoon outlet 10/1	na	na	na	na	na	na	na	na	4	1
Settling lagoon outlet 10/4	na	na	na	na	na	na	na	na	1	1
Settling lagoon outlet 10/5	na	na	na	na	na	na	na	na	2	2
Settling lagoon outlet 10/6	na	na	na	na	na	na	na	na	7	6

Table 7. Zeta potential, conductivity, and pH results for pulp NC processing wastewaters.

Sampling Location		Zeta P. mV	Cond. μmho/cm	pH
Boil. tub during load	after 0 min	na	na	1.7
	after 5 min	na	na	1.5
	after 30 min	na	na	1.4
Boil. tub after 20 hr boil	after 0 min	na	na	1.8
	after 5 min	na	na	1.7
	after 30 min	na	na	6.1
Boil. tub after 1st 5 hr boil	after 0 min	na	na	2.7
	after 5 min	na	na	2.7
	after 30 min	na	na	6.3
Boil. tub after 2nd 5 hr boil	after 0 min	na	na	1.8
	after 5 min	na	na	1.7
	after 30 min	na	na	2.1
Beater super. settled 1 hr		-16.70	216	7.9
Poach. super. settled 1 hr After 1 boil		-29.43	808	6.7
Poach. super. settled 1 hr After 3 boils		-29.47	565	6.6
Blender vac. drum tail water		-23.17	325	6.8
Blender super. settled 1 hr		-27.57	162	7.2
Wringer super. settled 1 hr		-22.83	147	7.4
Wringer super. settled 24 hr		-23.20	151	7.6
Wringer centrate, clean screen load		-19.17	158	7.4
Wringer centrate, caked screen load		-18.37	155	7.6

Table 8. Zeta potential, conductivity, and pH results for cotton NC processing wastewaters.

Sampling Location		Zeta P. mV	Cond. μmho/cm	pH
Boil. tub during load	after 0 min	na	na	1.4
	after 5 min	na	na	1.2
	after 30 min	na	na	1.2
Boil. tub after 20 hr boil	after 0 min	na	na	1.6
	after 5 min	na	na	1.7
	after 30 min	na	na	1.9
Boil. tub after 1st 5 hr boil	after 0 min	na	na	1.2
	after 5 min	na	na	1.3
	after 30 min	na	na	1.3
Boil. tub after 2nd 5 hr boil	after 0 min	na	na	3.5
	after 5 min	na	na	3.5
	after 30 min	na	na	6.4
Beater super. settled 1 hr		-18.77	149	7.1
Poach. super. settled 1 hr after 1 boil		-32.17	406	6.9
Poach. super. settled 1 hr after 2 boils		-31.43	366	6.7
Poach. super. settled 1 hr after 3 boils		-29.70	335	7.1
Poach. super. settled 1 hr after 1 boil		-33.97	446	6.8
Poach. super. settled 1 hr after 2 boils		-32.50	399	6.8
Poach. super. settled 1 hr after 3 boils		-31.07	297	6.9
Blender vac. drum tail water		-19.70	179	7.2
Blender super. settled 1 hr		-25.03	152	7.3
Blender super. settled 7 days		-22.57	166	7.1
Wringer super. settled 1 hr		-25.80	127	7.7
Wringer super. settled 13 days		-19.37	126	7.1
Wringer centrate, clean screen load		-25.43	137	7.6
wringer centrate, during wringing		-20.97	150	7.6
Wringer centrate, caked screen load		-19.83	143	7.7

The turbidity results were strongly correlated with the TSS results, being low for the boiling tub, boiling tub settling pit, basin 3054, hill tank effluent, DeLaval centrifuge centrate, neutralization basin, and settling lagoon samples, and high for the various tub supernatant and poacher settling pit samples.

The surface charges of the fine particles in the NC processing wastewaters were negatively charged, as expected. The magnitudes of surface charges on colloidal particles are commonly divided as follows: zero to 5 mV is slightly charged, 5 to 20 mV is moderately charged, and above 20 mV is highly charged. Since the zeta potentials for all the pulp and cotton processing wastewater samples were measured to be between -16 and -34 mV, the NC fine particles can be characterized as having moderately high to very high surface charges. The particles in the poacher, blender, and wringer supernatant samples were generally more highly charged than the remaining samples.

Table 9. Zeta potential, conductivity, and pH results for Basin 3054, boiling tub settling pit, and Hill Tank effluent.

Sampling Location	Zeta P. mV	Cond. μmho/cm	pH
Basin 3054 inlet 9/30	na	24000	1.4
Basin 3054 inlet 10/1	na	6940	1.9
Basin 3054 inlet 10/4	na	5880	1.9
Basin 3054 inlet 10/5	na	11960	1.7
Basin 3054 inlet 10/6	na	14410	1.6
Boiling tub settling pit inlet 9/30	na	122	5.2
Boiling tub settling pit inlet 10/1	na	34000	1.3
Boiling tub settling pit inlet 10/4	na	4310	2.0
Boiling tub settling pit inlet 10/5	na	25100	1.4
Boiling tub settling pit inlet 10/6	na	27300	1.3
Boiling tub settling pit outlet 9/30	na	2790	2.2
Boiling tub settling pit outlet 10/1	na	30500	1.4
Boiling tub settling pit outlet 10/4	na	7620	1.8
Boiling tub settling pit outlet 10/5	na	24300	1.4
Boiling tub settling pit outlet 10/6	na	24300	1.5
Recovered water tank effluent 8/26	na	172	7.2
Recovered water tank effluent 8/27	na	222	6.9
Recovered water tank effluent 8/31	na	179	7.8
Recovered water tank effluent 9/1	na	167	7.4

Table 10. Zeta potential, conductivity, and pH results for poacher settling pit and DeLaval centrifuge centrate.

Sampling Location	Zeta P. mV	Cond. μmho/cm	pH
Poacher pit inlet 8/26	-19.27	182	7.4
Poacher pit inlet 8/27	-16.57	153	7.8
Poacher pit inlet 8/31	-16.33	166	7.8
Poacher pit inlet 9/1	-21.27	145	8.0
Poacher pit outlet 8/26	-20.60	289	7.4
Poacher pit outlet 8/27	-17.73	163	7.3
Poacher pit outlet 8/31	-16.53	166	8.5
Poacher pit outlet 9/1	-19.97	145	7.9
Centrifuge centrate 8/26	-23.70	174	7.4
Centrifuge centrate 8/27	-14.37	185	7.1
Centrifuge centrate 8/31	-26.97	167	8.0
Centrifuge centrate 9/1	-19.37	145	8.0

Table 11. Zeta potential, conductivity, and pH results for neutralization basin and settling lagoon.

Sampling Location	Zeta P. mV	Cond. μmho/cm	pH
Neutralization basin inlet 9/30	na	5830	1.9
Neutralization basin inlet 10/1	na	8630	1.8
Neutralization basin inlet 10/4	na	2610	2.3
Neutralization basin inlet 10/5	na	3530	2.2
Neutralization basin inlet 10/6	na	1210	2.6
Neutralization basin outlet 9/30	na	1330	5.8
Neutralization basin outlet 10/1	na	2120	6.5
Neutralization basin outlet 10/4	na	660	6.4
Neutralization basin outlet 10/5	na	1144	4.9
Neutralization basin outlet 10/6	na	1250	5.3
Settling lagoon inlet 9/30	na	290	6.0
Settling lagoon inlet 10/1	na	270	6.0
Settling lagoon inlet 10/4	na	160	6.7
Settling lagoon inlet 10/5	na	240	6.3
Settling lagoon inlet 10/6	na	310	6.3
Settling lagoon outlet 9/30	na	1920	5.0
Settling lagoon outlet 10/1	na	1980	5.9
Settling lagoon outlet 10/4	na	280	6.3
Settling lagoon outlet 10/5	na	1470	5.9
Settling lagoon outlet 10/6	na	950	5.8

The conductivities of the wastewaters from the boiling tubs and nitrator were high due to high acid content. The conductivities of the various tub supernatants were generally lower, although adding soda ash during the first boil in the poacher tubs significantly increased the conductivities of the poacher tub supernatants. In general, the pHs of all the samples were near neutral except for the boiling tub, boiling tub settling pit, basin 3054, and neutralization basin influent samples, which had pHs in the range of 1 to 3. Detailed wastewater characteristics for each sampling location are discussed in the following sections.

Boiling Tub Drain

The PSD results for the boiling tub samples are listed as not available (na) due to very poor reproducibility in replicate analyses. This poor reproducibility can be attributed to the fact that these wastewater samples had low suspended solids concentrations, thus just a few larger particles in the 2 mL aliquot analyzed by the Brinkmann PSA could drastically change the PSD results. However, visual inspection of these samples showed that the small amount of solids present tended

to be larger particles that readily settled. This observation was supported by the low turbidity measurements for these samples, which indicated low concentrations of small NC fine particles. The boiling tub samples had TSS concentrations ranging from zero to 43 mg/L. The results show that the TSS concentrations in the boiling tub samples were greatest just after opening the drain ("after zero min"). This supports the operators' belief that, after a short period of time, a mat of NC forms at the orifices of the boiling tub false bottom that then prevents the discharge of additional NC. The boiling tub samples consistently had turbidities below 10 NTU. The zeta potential results for the boiling tub samples are listed as "na" because replicate analyses yielded extremely poor reproducibility. This poor reproducibility can again be attributed to the fact that these wastewater samples had low suspended solids concentrations. The conductivity results for the boiling tub samples are also listed as "na" because the pHs of these samples were increased with sodium hydroxide before shipping and then decreased to the original pHs with sulfuric acid after shipping; consequently conductivity measurements would have been meaningless. The pHs of the boiling tub samples, as measured at the plant, typically ranged from 1 to 3.

Beater House Dewatering Tub Supernatant

The PSD results for the beater dewatering tub samples indicated that >80 percent of the particles in the pulp NC supernatant were below 10 μm in size, but that the particles in the cotton NC supernatant ranged from zero to 100 μm; i.e., the particles in the pulp NC supernatant were on average smaller than in the cotton NC supernatant. This difference could possibly be attributed to differences in the physical structure of the pulp and cotton NC particles, i.e., the suspended cotton particles might be more fibrous-like. However, this simple interpretation is complicated by the fact that the pulp and cotton NC supernatants had TSS concentrations of 118 and 108 mg/L and turbidities of 75 and 592 NTU, respectively. These observed values would suggest that the NC particles in the pulp NC supernatant sample were actually larger, on average, than in the cotton NC supernatant sample. This conflict in interpretations of the empirical data could possibly be resolved by attributing the high TSS concentration in the pulp NC supernatant to a relatively small number of large particles (e.g., >100 μm) that were not analyzed in the 2 mL aliquots used for the PSD analyses. This interpretation was supported by a visual inspection of the samples, which showed the pulp NC supernatant to be clear with a small amount of larger particles settled on the bottom and the cotton NC supernatant to be cloudy with a very thin layer of fines settled at the bottom. The pulp and cotton NC supernatant had zeta potentials of -16.70 and -18.77 mV, respectively. The pulp and cotton NC supernatants had conductivities and pHs of 216 and 149 μmho/cm, and 7.9 and 7.1, respectively.

Poacher Tub Supernatant

The PSD results for the poacher tub samples indicated that >80 percent of the particles in both the pulp and cotton NC supernatants were below 10 μm in size. All the poacher tub supernatants that were sampled had been settled for approximately 1 hour. The TSS concentrations in the pulp NC supernatants were 139 and 183 mg/L, while the TSS concentrations in the cotton NC supernatants were higher, ranging from 340 to 601 mg/L. The turbidities of both the pulp and cotton NC supernatants were always greater than 1000 NTU. The zeta potentials of the pulp NC supernatants were both -29 mV, while the zeta potentials of the cotton NC supernatants ranged from -31 to -34 mV. The pulp NC supernatants had conductivities of 808 and 565 μmho/cm, while the cotton NC supernatants ranged from 446 to 297 μmho/cm. The poacher tub supernatant conductivities were always greatest after the first boil when soda ash was added. The pHs of all the poacher tub supernatants samples ranged from 6.6 to 7.1.

Blender House Vacuum Drum Tail Water

The PSD results for the blender house vacuum drum tail water indicated that approximately half the particles in both the pulp and cotton samples were greater than 30 μm in size. The larger particle sizes in the vacuum drum tail water may be attributed to the fact that solids are not settled out prior to discharge, i.e., the water is drained from the bottom of the tub, not decanted off the top. The TSS and turbidities of the pulp and cotton NC vacuum drum tail water samples were 290 and 77 mg/L, and >1000 and 47 NTU, respectively. It is possible that these dissimilarities between the pulp and cotton NC wastewater could, again, be due to differences in the structure of the pulp and cotton NC particles. The zeta potentials of the pulp and cotton NC vacuum drum tail water samples were -23 and -20 mV, respectively. The pulp and cotton NC vacuum drum tail water samples had conductivities and pHs of 325 and 179 μmho/cm, and 6.8 and 7.2, respectively.

Blender Tub Supernatant

The PSD results for the blender tub samples indicated that >90 percent of the particles in all the pulp and cotton NC supernatants were below 10 μm in size. The TSS concentrations in the pulp and cotton NC supernatants that had been settled approximately 1 hour were 433 and 555 mg/L, respectively, while the TSS concentration in the cotton NC supernatant that had been settled for 7 days was a much lower 155 mg/L (a 72 percent decrease). Since the 1-hour settled supernatants were not completely cooled, the higher TSS concentrations may have been due to temperature gradient-induced turbulence that kept the NC fines in suspension. The

turbidities of all the blender tub supernatants were greater than 1000 NTU. The zeta potentials of the 1-hour settled pulp and cotton NC supernatants were -28 and -25 mV, respectively, while the zeta potential of the 7-day settled cotton NC supernatants was -23 mV. The pulp NC supernatant had a conductivity of 162 µmho/cm, while the cotton NC supernatant conductivities were 152 and 166 µmho/cm. The pHs were 7.2, 7.3, and 7.1, respectively.

Wringer Storage Tub Supernatant

The PSD results for the wringer storage tub samples indicated that >85 percent of the particles in all the pulp and cotton NC supernatants were below 10 µm in size. The TSS concentrations in the pulp and cotton NC supernatants that had been settled approximately 1 hour were 286 and 338 mg/L, respectively. However, the TSS concentrations in the pulp NC supernatant that had been settled for 1 day and the cotton NC supernatant that was settled for 13 days were a much lower 112 and 81 mg/L, respectively (61 and 76 percent lower than the 1-hour settled samples). The higher TSS concentrations in the 1-hour settled supernatants may again have been due to the tubs not being completely cooled. The turbidities of the 1-hour settled pulp and cotton supernatants were both greater than 1000 NTU, as was the 1 day settled pulp supernatant. However, the turbidity of the cotton NC supernatant that had been settled for 13 days was only 105 NTU. The zeta potentials ranged from -19 to -26 mV, the conductivities ranged from 126 to 151 µmho/cm, and the pHs ranged from 7.1 to 7.7.

Wringer Centrate

The PSD results for the wringer centrate samples indicated that the NC particles were widely distributed from zero to >100 µm. The larger sizes can again probably be attributed to the fact that the particles are not settled out before being discharged to the poacher pits. The TSS concentrations in the pulp and cotton NC centrate during a loading of a clean screen were 385 mg/L and a very high 3660 mg/L, respectively. The TSS concentration in the cotton NC centrate during the actual wringing process was 120 mg/L. A sample of the pulp NC centrate during the actual wringing could not be collected due to the low discharge flows generated. The TSS concentrations in the pulp and cotton NC centrate during a load of a caked screen (with a thin layer of NC from the previous load adhered to the screen) were a much lower 40 and 27 mg/L, respectively. Obviously, the existence of a layer of NC on the wringer screens helps to prevent the loss of NC to the poacher pits. The turbidities of the pulp and cotton NC centrate during a clean screen load were 333 and >1000 NTU, respectively. The turbidity of the cotton NC centrate during wringing was 470 NTU. The turbidities of the pulp and cotton NC centrate during a caked screen load

were a much lower 12 and 15 NTU, respectively. The zeta potentials ranged from -18 to -25 mV, the conductivities ranged from 137 to 158 mg/L, and the pHs ranged from 7.4 to 7.7.

Boiling Tub Settling Pit Inlet and Outlet

During the period when samples were collected from the C-line boiling tub settling pits, wastewater was being received from the boiling tub house only (Figure 12). Note that the boiling tub settling pits also often receive wastewater from the nitrator and the recovered water tanks (Figure 11). Samples were collected at the boiling tub settling pit from just below the water surface at the inlet and outlet ends. The inlet samples were not true influent samples since some NC undoubtedly settles out immediately after the wastewater is discharged to the settling pits.

The boiling tub settling pit samples were all very clear with very little visible solids content. The PSD and zeta potential results for the boiling tub settling pit samples are listed as "na" because replicate analyses yielded extremely poor reproducibility due to low suspended solids concentrations. The TSS concentrations of the inlet samples ranged from zero to 20 mg/L, while the outlet samples ranged from 1 to 9 mg/L. The turbidities of the inlet samples ranged from zero to 2 NTU, while the outlet samples ranged from 1 to 6 NTU. The conductivities of the inlet samples ranged from 122 to 34,000 μmho/cm, while the outlet samples ranged from 2790 to 30,500 μmho/cm. The pHs of the inlet samples ranged from 1.3 to 5.2, while the outlet samples ranged from 1.4 to 2.2. The lower conductivities and higher pHs observed in the inlet samples undoubtedly corresponded to a day when no wastewater was being discharged to the settling pit from either the nitrator or from boiling tubs before or after an acid boil.

Settling Basin 3054 Inlet

During the second sampling period, settling basin 3054 received wastewater from the nitrator (Figure 12). Samples were collected at basin 3054 from just below the water surface at the inlet only. The samples were all very clear with a very small amount of large settled solids. The PSD and zeta potential results are listed as "na" because replicate analyses yielded extremely poor reproducibility due to the very low suspended solids concentrations. However, the visual appearance of basin 3054 samples indicates that the NC particles were generally fairly large (e.g., >100 μm). The TSS concentrations ranged from 2 to 12 mg/L, and the turbidities ranged from 1 to 6 NTU. The conductivities ranged from 5880 to 24,000 μmho/cm, while the pHs ranged from 1.4 to 1.9.

Poacher Settling Pit Inlet and Outlet

The samples were taken from the poacher settling pit just below the water surface at the inlet end and just past the dam (Figure 12) at the outlet end. The inlet samples were again not true influent samples, since some NC undoubtedly settles out immediately. The PSD results indicated that particles in the poacher pit inlet and outlet were distributed over a range of zero to >100 µm. The larger particle sizes can be attributed to the poacher pit receiving unsettled wastewater from the wringer filtrate and the vacuum drum tail water, and also to the practice of discharging the DeLaval centrifuge backflush water back into the poacher pits. The TSS concentrations in the poacher pit inlet samples ranged from 53 to 250 mg/L, while the outlet samples ranged from 107 to 171 mg/L. The turbidities of the poacher pit inlet ranged from 17 to >1000 NTU, while the outlet ranged from 37 to 470 NTU. The conductivities and pHs of the settling pit samples ranged from 145 to 289 µmhos/cm and 7.3 to 8.5, respectively. Finally, it should be noted that shortly after the sampling survey was conducted, excessive amounts of NC were observed to be accumulating in the poacher pit, much to the dismay of one of the operators. The source of the excessive NC loading was not known to the operator, but it may have been due to an upset caused by a switch in manufacturing lines.

DeLaval Centrifuge Centrate and Recovered Water Tank Effluent

The effluent from the poacher pits is pumped through the DeLaval sliding bowl centrifuges. The centrifuge centrate is then pumped to the recovered water tanks (hill tanks), while the backflush water containing the removed NC is returned to the poacher pits. The effluent from the recovered water tanks flows to the boiling tub settling pits. Some settling of NC fines occurs in the recovered water tanks, as is evident from the accumulation of NC at the bottom of the tanks estimated by Balasco et al. (1987) to be 400,000 lb for Tank #1 and 70,000 lb for Tank #2 in 1987. The PSD and zeta potential results for the DeLaval centrifuge centrate and recovered water tank effluent samples are listed as “na,” again due to very poor reproducibility in replicate analyses caused by low suspended solids concentrations. However, these wastewater streams would be expected to have predominantly smaller particles (<10 µm), since larger particles are preferentially removed by the centrifuges. The TSS for the DeLaval centrate samples ranged from 4 to 17 mg/L, while the recovered water tank effluent samples ranged from 3 to 13 mg/L. The turbidities of the centrifuge centrate samples ranged from 4 to 13 NTU, while the recovered water tank effluent samples ranged from 3 to 5 NTU. The conductivities of the centrifuge centrate and recovered water tank effluent samples ranged from 145 to 222 µmhos/cm. The pH ranged from 6.9 to 8.0.

Neutralization Basin Influent and Effluent

The PSD and zeta potential results for the neutralization basin samples are listed as "na" due to poor reproducibility between replicate analyses caused by the low suspended solids concentrations. The TSS concentrations for the neutralization basin influent samples ranged from 2 to 13 mg/L, while the effluent samples ranged from 6 to 62 mg/L. The higher TSS concentrations for the effluent samples probably resulted from the formation of calcium sulfate and other precipitates due to the addition of lime. The turbidities for the influent samples ranged from 4 to 16 NTU, while the effluent samples ranged from 3 to 25 NTU. The conductivities of the neutralization basin influent samples were fairly high (1210 to 8630 µmho/cm), while the conductivities of the effluent samples were somewhat lower (660 to 2120 µmho/cm), probably due to the acid neutralization. The pHs of the influent samples ranged from 1.8 to 2.6, while the effluent samples ranged from 4.9 to 6.5.

Settling Lagoon Influent and Effluent

The PSD and zeta potential results for the settling lagoon samples are also listed as "na" due to poor reproducibility between replicate analyses caused by the low suspended solids concentrations. The TSS concentrations in the settling lagoon influent samples ranged from 3 to 5 mg/L, while the effluent samples ranged from 1 to 7 mg/L. The TSS concentrations of the settling lagoon influent are less than those for the neutralization basin because the settling lagoons receive wastewater from other sources as well. Note that the suspended solids in the settling lagoon effluent samples were green, indicating the presence of algae. The turbidities of the settling lagoon influent samples ranged from 3 to 4 NTU, while the effluent samples ranged from 1 to 7 NTU. The conductivities of the settling lagoon influent samples ranged from 160 to 310 µmho/cm, while the effluent samples ranged from 280 to 1980 µmho/cm.

Comparison to Previous NC Wastewater Characterization Studies

Tables 12, 13, and 14 show PSD and TSS results obtained in previous studies (Heffinger and Worrell 1992; Peng et al. 1992; and Dehart and Musser 1993). The previous PSD measurements were made by passing the wastewater samples through filters of decreasing pore size, whereas the PSD measurements were made in this study using the Brinkmann PSA. It should be noted that the average TSS concentrations listed in Table 14 were actually back-calculated from cited mass loading and flow rates.

Table 12. 1991 RAAP study particle size distribution and TSS results.

	% by weight in the indicated range (μm)					TSS
Sample	0.45-44	44-75	75-105	105-420	>420	(mg/L)
Boiling tub settling pit influent	71	0	0	29	0	45
Boiling tub settling pit effluent	65	4	8	22	1	30
Poacher settling pit influent	54	4	2	31	10	458
Poacher settling pit effluent	90	3	2	4	1	148
DeLaval centrifuge centrate	87	4	4	4	2	72
Neutralization basin influent	64	6	2	15	13	25
Settling lagoon effluent	64	1	0	4	31	26

Table 13. 1992 UW study particle size distribution results.

	% by weight in the indicated range (μm)						
Sample	0.45-10	10-20	20-30	30-41	41-70	70-210	>210
Poacher settling pit effluent	26	69	3	0	1	1	1

Also note that the calculated average TSS concentrations for the RAAP study (1993) were not completely consistent with the reported range of TSS concentrations, e.g., the average TSS concentration for the beater tub cotton NC supernatant was calculated to be 4 mg/L, but the range was reported as 10 to 120 mg/L. Finally, note that the Hercules study (Dehart and Musser 1993) did not sample the blender house vacuum filter tailwater or the wringer storage tub supernatant, nor did it distinguish between the TSS concentrations for the wringer centrate during clean screen loading, caked screen loading, and the actual wringing process.

The following observations result from comparing the PSD and TSS results from the previous studies (Tables 12 to 14) to the result of this study (Tables 2 to 6):

1. The Hercules (Heffinger and Worrell 1992) study and this study complement each other. The Hercules (1992) study reported PSD results for several locations that were "na" in this study: boiling tub settling pit, DeLaval centrifuge centrate, recovered water tank effluent, neutralization basin, and settling lagoon. This is because of the different measurement techniques used,

Table 14. 1993 RAAP study TSS results.

Sample	Ave. TSS (1) (mg/L)	TSS range (2) (mg/L)
Boiling tub drain-pulp NC	44	na
Boiling tub drain-cotton NC	43	na
Beater tub supernatant-pulp NC	4	6-11
Beater tub supernatant-cotton NC	4	10-120
Poacher tub supernatant-pulp NC	347	300-640
Poacher tub supernatant-cotton NC	342	300-600
Blender tub supernatant-pulp NC	461	na
Blender tub supernatant-cotton NC	429	na
Wringer centrate-pulp NC	168	155-230
Wringer centrate-cotton NC	72	105-135

(1) As calculated from pp. 20 and 61-62 of 1993 report by M.G. DeHart.
(2) As determined from 12 samples (Figures 33, 37, 45, 51, 57, and 63 of 1993 report by M.G. DeHart).

i.e., the automatic PSA used in this study was found to provide unreliable PSD measurements at low suspended solids concentrations. Also note that the Hercules (1992) study found significant percentages (>23 percent) of the NC particles to be larger than 105 µm in the boiling tub settling pit influent and effluent, the poacher settling pit influent, the neutralization basin influent, and the settling lagoon effluent. Similarly, this study found the poacher settling pit inlet and outlet samples to have significant percentages (~17 and 13 percent, respectively) of the NC particles greater than 100 µm.

2. The Hercules study (1992) found that >65 percent of the particles in the boiling tub settling pit influent and effluent were below 44 µm in size. While this study did not obtain reliable PSD results for samples from the boiling tub settling pit, samples from these locations were found to have very low turbidities and visual inspection showed them to be very clear with small amounts of large settled particles. This suggests that, in this study, the particles from the boiling tub settling pits were probably predominantly >44 µm in size (based on total volume, not number). However, note that the boiling tub settling pit was not receiving flow from the recovered water tanks during sampling for this study, which could easily account for the fact that smaller particles were not observed.

3. The Hercules (1992) study and the UW (1992) study found that >90 percent of the particles in the poacher pit effluent were below 40 µm in size. However, this study found that, on average, only about 60 percent of the particles in the poacher pit effluent were below 44 microns in size. This could be attributable to an unusually high proportion of the total flow to the poacher pits coming from the wringer house during this study (due to the switch-over in production lines). Since the wringer house wastewater was found to contain larger sized NC particles, this would have resulted in a higher than normal concentration of larger NC particles in the poacher pits. As previously discussed, it is also possible that the Brinkmann PSA used in this study yielded different results than would have been obtained using the filtration method used in the previous studies.

4. The Hercules (1992) study found higher TSS concentrations than this study for all the sampled wastewater treatment locations except the poacher settling pit effluent. The boiling tub settling pit influent and effluent concentrations were 45 and 30 mg/L versus zero to 20 and 1 to 9 mg/L, the poacher settling pit influent concentrations were 458 versus 53 to 250 mg/L, the DeLaval centrate concentrations were 72 versus 4 to 17 mg/L, the neutralization basin influent concentrations were 25 versus 2 to 13 mg/L, and the settling lagoon effluent concentrations were 26 versus 1 to 7 mg/L. It is possible that the lower TSS concentrations found during this study were due to lower overall NC production rates resulting from manufacturing line-B being switched over to C-line. In addition, the UW study did not actually sample the composite influent to the boiling tub and poacher settling pits, but rather collected samples from within the basins near the inlets. Consequently, the measured TSS concentrations of these samples were probably lower than for the actual composite influent for these locations. Finally, the boiling tub settling pit that was sampled during this study was not receiving flow from the recovered water tank.

5. The Hercules (1993) study and this study found comparable TSS concentrations for the poacher, blender, and wringer house wastewaters. The Hercules (1993) study reported slightly higher TSS concentrations for the boiling tub drain wastewater than were generally found in this study (44 mg/L versus 0 to 43 mg/L). In addition, the Hercules (1993) study reported the average TSS concentrations for the beater house dewatering tub to be approximately 4 mg/L whereas this study found the average TSS concentration to be approximately 110 mg/L. However, note that the Hercules (1993) study reported the range of TSS concentrations for the beater dewatering tub to be 6 to 11 mg/L for the pulp NC supernatant and 10 to 120 mg/L for the cotton NC

supernatant. This suggests that the average TSS of 4 mg/L reported in the Hercules (1993) report may have been erroneous, and also indicates that there is a wide range in the TSS concentrations for the beater dewatering tub supernatant. The Hercules (1993) study did not obtain TSS concentrations for the blender house rotating vacuum filter tail water or the wringer house storage tub supernatant.

Mass Balance Estimations

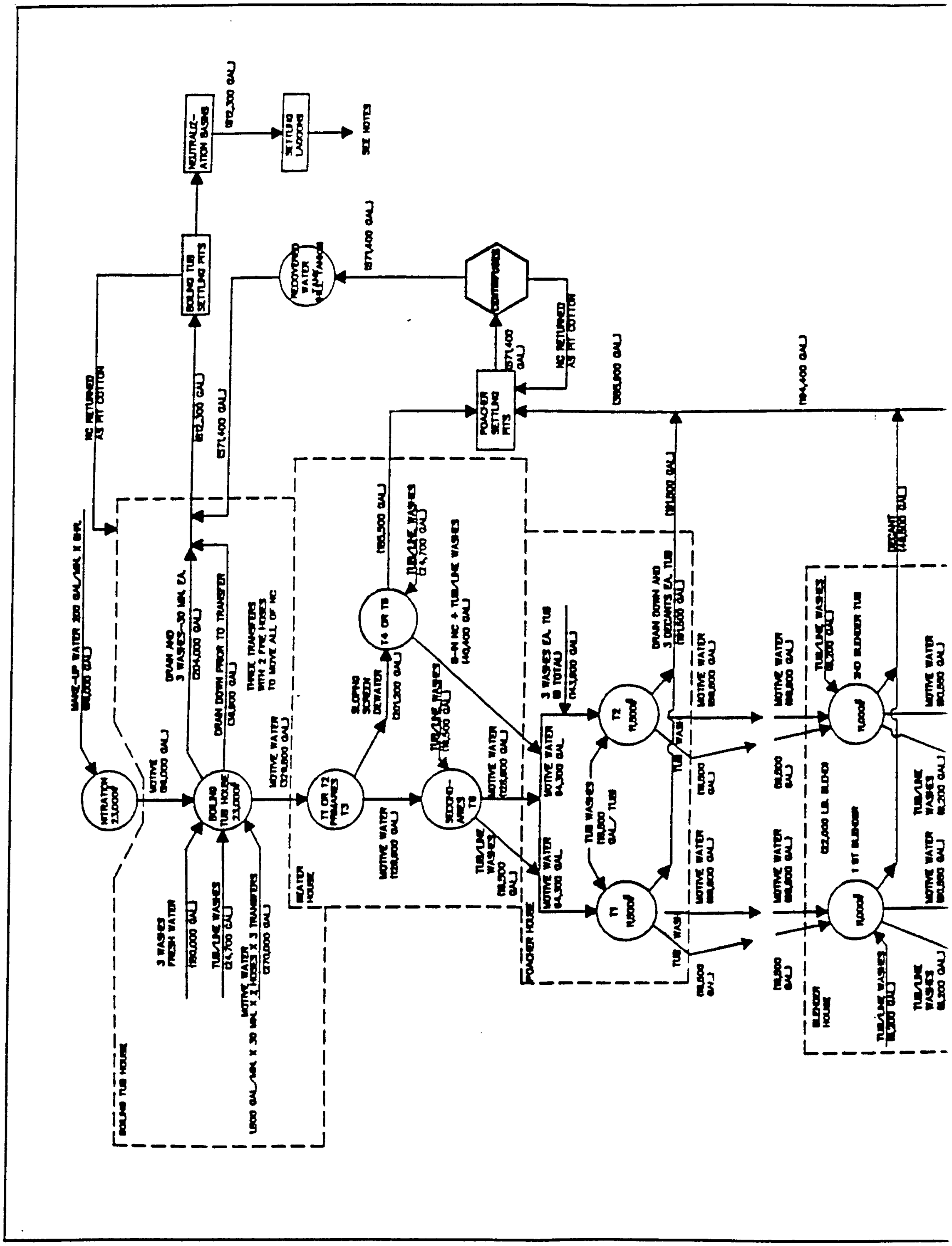
The mass of NC discharged to the settling pits from the five processing operations (boiling tub house, beater house, poacher house, blender house, and wringer house) during both pulp and cotton NC processing were estimated using the TSS measurements made in this study (listed in Tables 2 to 6) and water balances determined in a previous study as shown in Figures 13 and 14 (Hercules 1993). These mass balance estimations are shown in Tables 15 and 16.

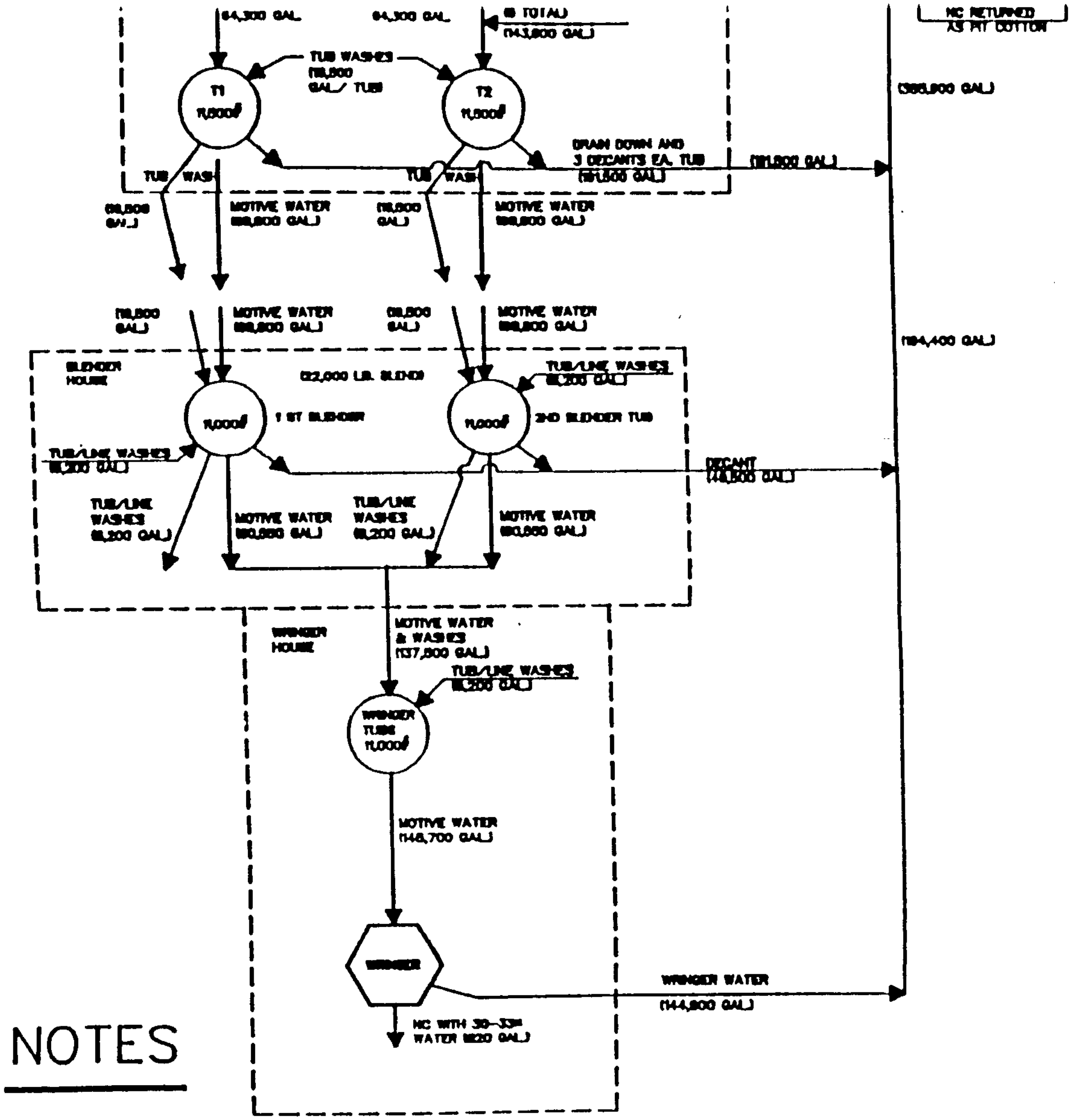
It should be noted that these mass balance calculations were very crude estimations based on rough flow approximations and one-time TSS measurements. The water use rates at the various NC processing vary over a wide range, depending on the skills of the operators, the weather, and the types and final blends of NC being produced. For example, the number of transfers required to move all of the NC out of a boiling tub depends, in part, on the skill of the operators in using fire hoses to divide the material and to flush it through the piping to the beater house without plugging the lines. Also, during freezing weather, filtered water is allowed to flow continuously in many areas for freeze protection. Thus, the flow diagrams shown in Figures 13 and 14 were developed on best engineering estimates taking this variability into account (Hercules 1993). Also note that these flow diagrams neglect to cite flow rates from the rotating vacuum filters in the blender house, as well as from the wringer house storage tub decants; the diagrams also do not cite specific flow rates from the wringers during clean and caked screen loading as well as the actual wringing process. Also, the TSS concentrations in the various wastewater streams vary over a wide range, depending on such factors as the time tubs are allowed to settle before being decanted, the condition of the perforated heads at the top of the decant pipes (at a few tubs these strainer heads were absent altogether), and the flow variability discussed above.

The results shown in Tables 15 and 16 show that the boiling tub house was estimated to have by far the lowest NC mass loading to the settling pits, while the poacher house was estimated to have the greatest. Also, the cotton NC processing wastewaters were estimated to discharge almost twice as much NC to the settling

pits as the pulp NC processing wastewaters (per ton of NC processed). The pulp and cotton NC mass loadings to the settling pits were estimated to be 66.2 and 113.4 lb per ton of NC processed, or approximately 3.31 and 5.67 percent of the initial mass of NC being treated, respectively. The pulp and cotton NC mass loadings ultimately lost to the neutralization basin were estimated to be 5.0 and 4.7 lb per ton of NC processed, or approximately 0.25 and 0.24 percent, respectively, of the initial mass of NC being processed. Assuming the differences between the mass loadings to the settling pits and to the neutralization basin were completely attributable to recycling NC from the settling pits as "pit cotton," the masses of pulp and cotton NC recycled per ton of NC processed were estimated to be 61.2 and 108.7 lb, or 3.1 and 5.4 percent, respectively, of the initial mass of NC being processed.

According to the mass balance estimations above, the percentages of the pulp and cotton NC discharged to the settling pits that end up being recycled as pit cotton are 92.4 and 95.9 percent, respectively. The current use of pit cotton helps RAAP to not dispose of this low quality NC. However, the Army may terminate the use of pit cotton to improve the quality of propellent. When such time comes, NC disposal will be a very expensive and difficult task. During this study, the average TSS concentrations at the poacher pit inlet and outlet (Figure 2) were 148 and 133 mg/L, respectively, while the average DeLaval centrifuge centrate TSS concentration was 8 mg/L. From these measured TSS concentrations, the total NC removal between the poacher pit influent and the centrifuge centrate is calculated to be 94.6 percent (which compares well with the values of 92.4 and 96.0 percent above). Of this, 10.1 percent would appear to be attributable to settling in the poacher pit and the other 84.5 percent would appear to be attributable to removal by the DeLaval centrifuges. This is misleading, however, since the centrifuge backflush water containing the recovered NC is discharged back to the poacher settling pit, and thus some of the TSS in the poacher pit outlet will be NC that has already been previously cycled through the centrifuges. Thus, the NC removal efficiency that would be attained by the poacher pits without the centrifuges is probably greater than the 10.1 percent calculated above. However, note that the NC in the centrifuge backflush water is probably much more floc-like than the NC in the influent to the centrifuges and thus probably settles fairly well.


NEUTRALIZATION BASINS
SETTLING LAGOONS
SEE NOTES
BOILING TUB SETTLING PITS
RECOVERED WATER
CENTRIFUGES
NC RETURNED AS PIT COTTON
POACHER SETTLING PITS
NITRATION
BOILING TUB HOUSE
BEATER HOUSE
POACHER HOUSE
BLENDER HOUSE
1 ST BLENDER
2ND BLENDER TUB
MOTIVE WATER
TUB/LINE WASHES
DECANT



NOTES

A. 1992 PRODUCTION:
LINTERS: 17.4 TUBS/M X 812,300 GAL./TUB = 14,134,00 GAL/M
PULP: 15.37 TUBS/M X (1,231,700 GAL./TUB = 18,845,000 GAL./M

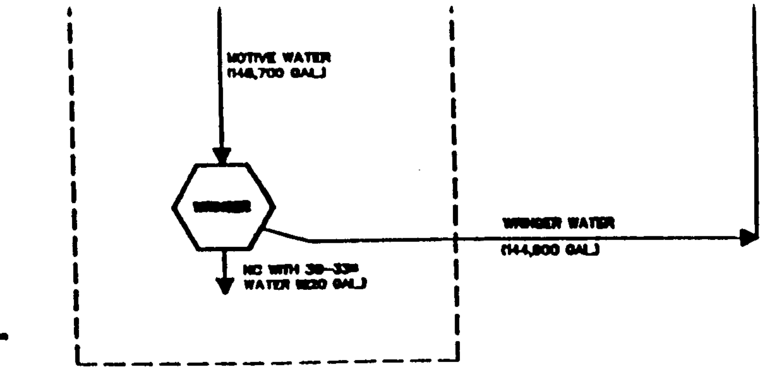
TOTAL: 32,979,100 GAL./M 20 DAYS/M=1,649,000 GAL./DAY

B. OUTFALLS 005 AND 007 HAD A COMBINED AVERAGE OF 3,883,000 GAL/DAY IN 1992.

C. ENGINEERING ESTIMATES THAT NC PRODUCTION ACCOUNTS FOR 40% OF WATER LEAVING OUTFALLS 005 AND 007 COMBINED

2

3



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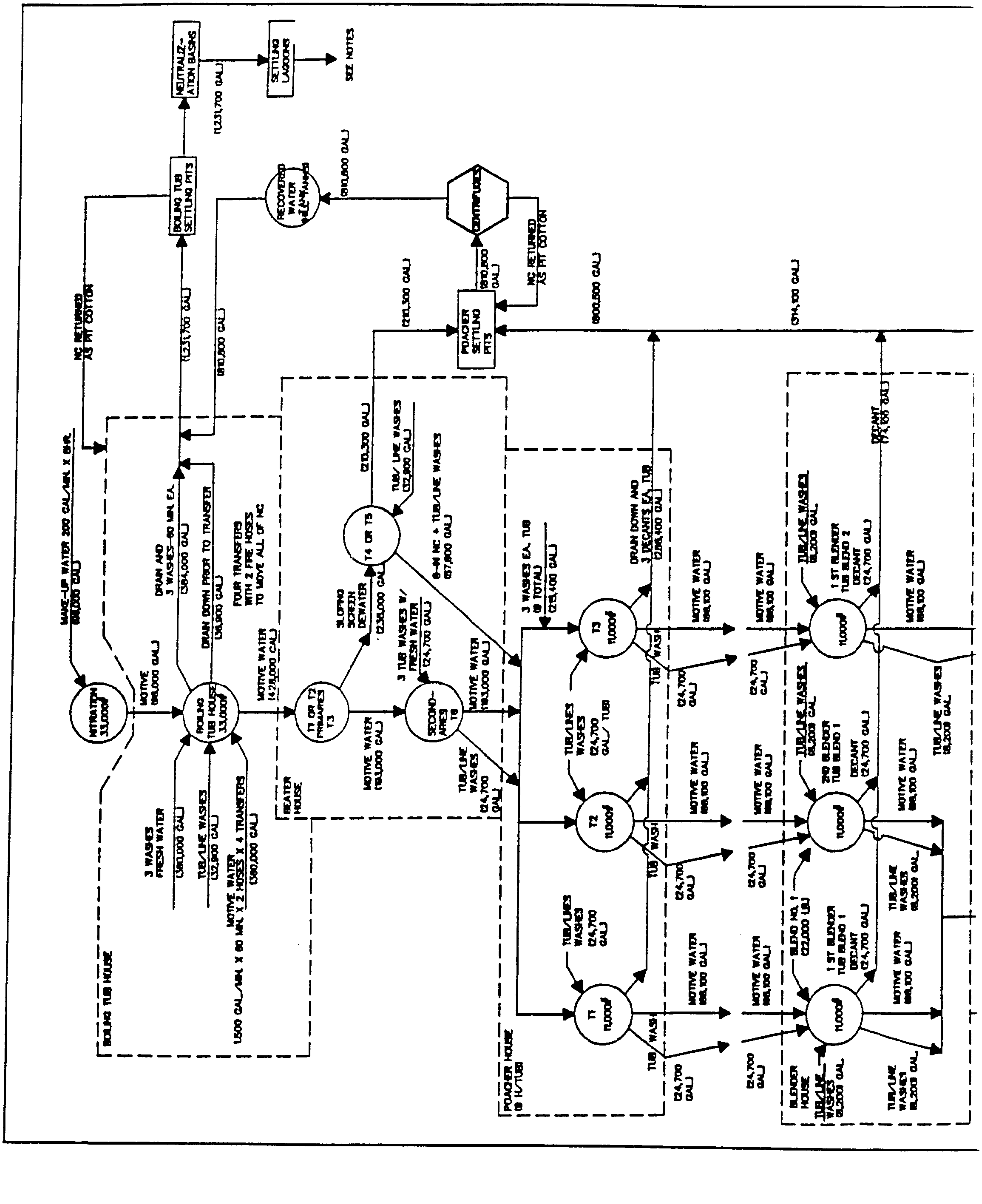
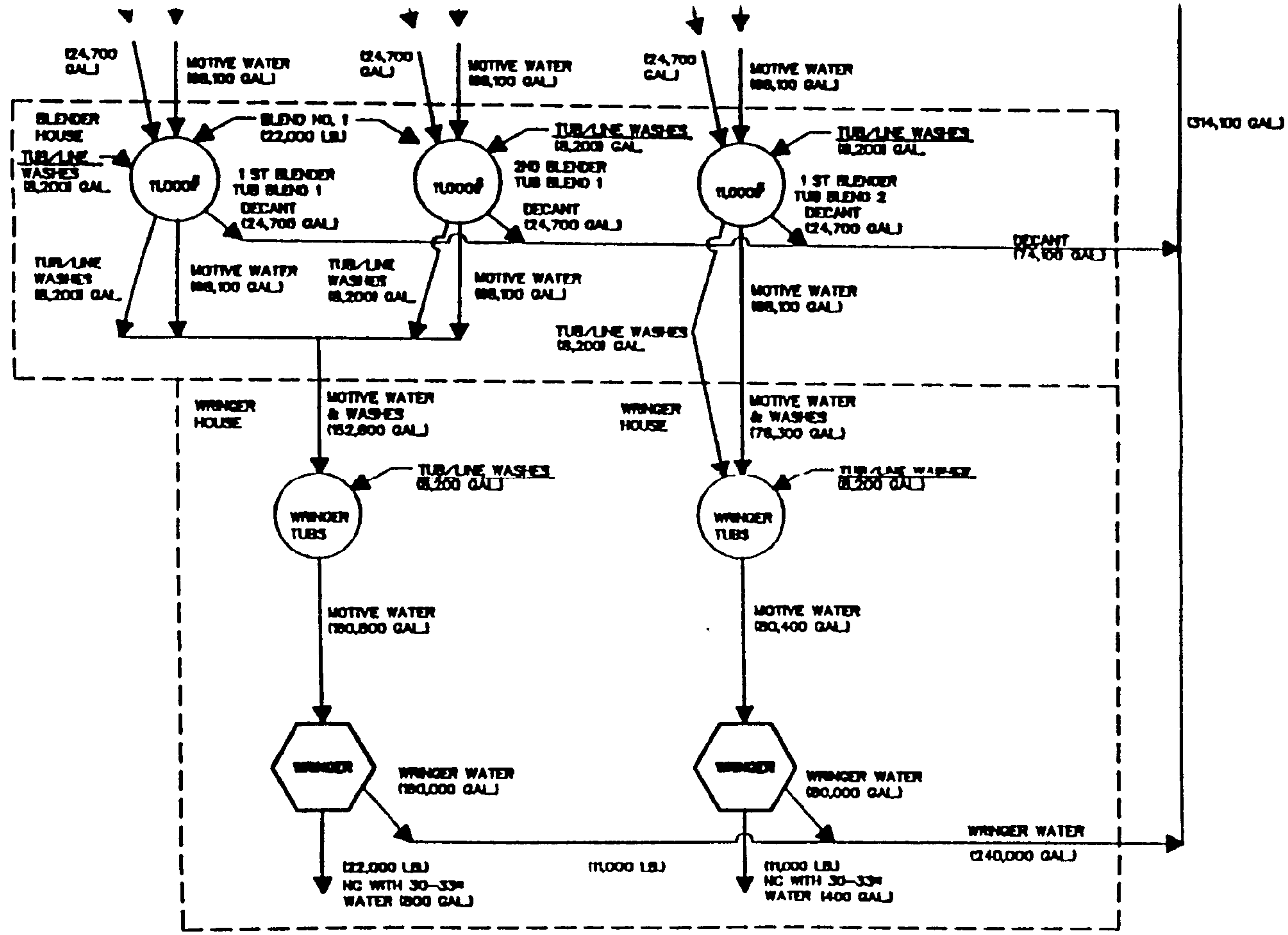
40% X 3,883,000 GAL./DAY= 1,550,000 GAL./DAY

REFERENCE DRAWING
50863 NIT. PULP PURFI. WATER BAL.

Figure 13. NC pulp purification water balance.


NITRATION 33,000#
BOILING TUB HOUSE 33,000#
BOILING TUB SETTLING PITS
NEUTRALIZATION BASINS
SETTLING LAGOONS
SEE NOTES
RECOVERED WATER
CENTRIFUGES
POACHER SETTLING PITS
NC RETURNED AS PIT COTTON
T1 OR T2 PRIMARIES T3
T4 OR T5
SECONDARIES T6
BEATER HOUSE
BOILING TUB HOUSE
POACHER HOUSE
BLENDER HOUSE
MOTIVE WATER
TUB/LINE WASHES
DECANT



NOTES

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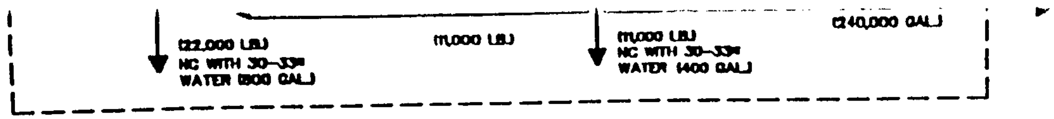
PULP: 15.37 TUBS/M X (1,231,700 GAL./TUB = 18,845,000 GAL./M
TOTAL: 31,272,600 GAL./M ÷ 20 DAYS/M=1,648,950 GAL./DAY

B. OUTFALLS 005 AND 007 HAD A COMBINED AVERAGE OF 3,883,000 GAL/DAY IN 1992.

C. ENGINEERING ESTIMATES THAT NC PRODUCTION ACCOUNTS FOR 40% OF WATER LEAVING OUTFALLS 005 AND 007 COMBINED.
40% X 3,883,000 GAL./DAY= 1,550,000 GAL./DAY

DRAWING REFERENCE
50654 NIT. COTTON LINTERS

2



NOTES

A. 1992 PRODUCTION:
LINTERS: 17.4 TUBS/M X 812,300 GAL./TUB = 14,134,000 GAL/M
PULP: 15.37 TUBS/M X (1,231,700 GAL./TUB = 18,845,000 GAL./M
TOTAL: 31,272,600 GAL./M ÷ 20 DAYS/M=1,648,950 GAL./DAY

B. OUTFALLS 005 AND 007 HAD A COMBINED AVERAGE OF 3,883,000 GAL/DAY IN 1992.

C. ENGINEERING ESTIMATES THAT NC PRODUCTION ACCOUNTS FOR 40% OF WATER LEAVING OUTFALLS 005 AND 007 COMBINED.
40% X 3,883,000 GAL./DAY= 1,550,000 GAL./DAY

DRAWING REFERENCE
50654 NIT. COTTON LINTERS

Figure 14. NC cotton purification water balance.

Table 15. Mass balance calculations for pulp NC (UW 1994).

NC processing operation	Ave. volume of waste-water per ton of NC processed (gal)	Average TSS of wastewater (mg/L)	Average mass of NC lost per ton of NC processed (lb)
Boiling tub house	25,509	10	2.1
Beater house	12,745	118	12.5
Poacher house	17,358	161	23.3
Blender house	4,491	433	16.2
Wringer house	14,545	100	12.1
Total to settling pits	74,648	106	66.2 (3.31%)
Total to neutral. Basin	~74,648	8	5.0 (0.25%)
Total recycled			61.2 (3.06%)

Table 16. Mass balance calculations for cotton NC (UW 1994).

NC processing operation	Average volume of wastewater per ton of NC processed (gal)	Average TSS of wastewater (mg/L)	Average mass of NC lost per ton of NC processed (lb)
Boiling tub house	20,948	11	1.9
Beater house	16,130	108	14.5
Poacher house	15,783	490	64.5
Blender house	4,304	555	19.9
Wringer house	12,600	120	12.6
Total to settling pits	69,765	195	113.4 (5.67%)
Total to neutral basin	~69,765	8	4.7 (0.24%)
Total recycled			108.7 (5.43%)

Comparison to Previous Mass Balance Estimations

Tables 17 and 18 show rough mass balances estimated in the Hercules study (1993). Comparison of Tables 17 and 18 to Tables 15 and 16 shows that the mass balance estimations made in the Hercules (1993) study and this study were quite comparable. However, note again that, since no wastewater flow estimations were made in this study, the flow rates used for the mass balance calculations were the same as those used in the Hercules (1993) study. Thus, the differences in the mass balance estimations between the two studies only reflect differences in the measured TSS concentrations.

Table 17. Mass balance calculations for pulp NC (DeHart 1993).

NC processing operation	Ave. volume of waste-water per ton of NC processed (gal)	Average TSS of wastewater (mg/L)	Average mass of NC lost per ton of NC processed (lb)
Boiling tub house	25,509	44	9.4
Beater house	12,745	4	0.4
Poacher house	17,358	347	50.2
Blender house	4,491	461	17.3
Wringer house	14,545	168	20.4
Total to settling pits	74,648	157	97.7 (4.89%)
Total to neutral basin	~74,648	30	18.7 (0.94%)
Total recycled			79.0 (3.95%)

Table 18. Mass balance calculations for cotton NC (DeHart 1993).

NC processing operation	Average volume of wastewater per ton of NC processed (gal)	Average TSS of wastewater (mg/L)	Average mass of NC lost per ton of NC processed (lb)
Boiling tub house	20,948	43	7.5
Beater house	16,130	4	0.5
Poacher house	15,783	342	45.0
Blender house	4,304	429	15.4
Wringer house	12,600	72	7.6
Total to settling pits	69,765	131	76.0 (3.80%)
Total to neutral basin	~69,765	30	17.5 (0.87%)
Total recycled			58.5 (2.92%)

The pulp and cotton NC losses to the settling pits were estimated to be 4.89 and 3.80 percent, respectively, in the Hercules (1993) study and 3.31 and 5.67 percent, respectively, in this study. Note that the Hercules (1993) study found that pulp NC losses (per unit mass of NC processed) were greater than cotton NC losses, whereas this study found that cotton NC losses were greater than pulp NC losses. The pulp and cotton NC ultimately lost to the final settling lagoons was estimated to be 0.94 and 0.87 percent, respectively, in the Hercules (1993) study, and 0.25 and 0.24 percent, respectively, in this study. The percentages of the pulp and cotton NC lost to the settling pits that are recovered as pit cotton were estimated to be 81 and 77 percent, respectively, in the Hercules (1993) study, and 92 and 96 percent,

respectively, in this study. It is possible that the better removal and recovery percentages observed in this study reflect the fact that the NC production was being switched from the A-B-line to the C-line, thus the total NC processing rates were lower than normal.

Both studies found that losses from the poacher house constituted the greatest NC loading to the settling pits, but that losses from the blender and wringer houses were also significant. The two studies obtained different results for the boiling tub and beater houses. The Hercules (1993) study reported the NC losses from the boiling tub house to be approximately four times that estimated in this study, and this study reported NC losses from the beater house to be approximately 30 times that estimated in the Hercules (1993) study. These discrepancies between the two studies are due to the differences in the observed TSS concentrations for the boiling tub drain wastewater (~44 mg/L in the Hercules 1993 study versus ~10 mg/L in this study) and the beater dewatering tub decant (~110 mg/L in this study versus ~4 mg/L in the Hercules 1993 study). It is suspected that the 4 mg/L TSS cited in the Hercules (1993) report for the beater dewatering tub decant was a typographical error.

Cationic Polymer and pH Adjustment Jar Tests

Based on a comparison of performance of numerous polymers, one polymer was selected for further evaluation. Table 19 shows the results of the jar tests conducted when Rhone-Poulenc C-4450 cationic polymer was added to poacher pit influent. The polymer reduced the turbidity of the poacher pit wastewater down to zero NTU within 15 minutes at the very low doses of 0.25 and 0.50 mg/L. (The final turbidity of the control sample was 153 NTU.) The flocs formed were quite large with excellent settling characteristics. Unfortunately, a compatibility test RAAP personnel performed with the C-4450 polymer showed that it was reactive with NC. When 0.25 grams of high grade HN-12 propellant was mixed with 0.25 grams of the C-4450 polymer and heated at 93 °C, the measured gas pressure went >200 mL of Hg within 30 minutes (the usual time of the compatibility test is 23 hours). This raises questions as to whether the polymer can be used to remove NC fines from the RAAP wastewater, and rules out recycling NC fines that have been settled out using the polymer. However, a wide variety of other cationic coagulants exist. It is likely that a substitute for the C-4450 polymer could be found that would not react with the NC. The poacher settling pits could be easily retrofitted for coagulation and flocculation.

Table 19. Jar test turbidity results (NTU) for Rhone-Poulenc C-4450 polymer.

	Polymer Concentration (mg/L)					
Turbidity at:	**0**	**0.10**	**0.25**	**0.50**	**1.00**	**5.00**
0 min.	410	410	410	410	410	410
5 min.	380	4	1	2	5	10
10 min.	220	2	1	1	4	7
15 min.	207	2	0	0	2	7
20 min.	173	2	0	0	2	5
25 min.	173	2	0	0	2	4
30 min.	153	2	0	0	2	3
Final pH	7.98	7.92	7.96	7.97	7.92	7.95

Table 20 shows the results of the first set of jar tests in which the pHs were adjusted by adding sulfuric acid or sodium hydroxide. A previous study (Peng et al. 1991) found the iso-electric point (the pH at which the surface charge is zero) for the NC fines to be approximately 1.9. It was therefore postulated that lowering the pH to about 2 would reduce the negative surface charges of the NC fines, and thus promote inter-particle conglomeration and settling. However, the results of the first set of pH adjusted jar tests shown below indicate that adjusting the pH of the poacher pit wastewater had no significant effect on the wastewater's turbidity. Since the initial pH of the wastewater was an uncharacteristically low 5.5, this may have somehow adversely affected the particle surface chemistry. It should be noted that the wastewater was shipped and stored in a nearly head-space-less container, and thus the low pH should not have been due to dissolution of atmospheric CO_2.

Since the first set of pH adjusted jar tests did not produce the expected results, a second trial was performed using poacher pit influent that had been previously shipped to the UW for other lab tests. The initial pH of this NC wastewater was a more characteristic 7.7. The results of the second set of pH adjusted jar tests are shown in Table 21. These results show that low turbidities were attained at pHs of 2.0 and 2.5, as anticipated. The iso-electric point for this NC wastewater was determined to be approximately 1.7, supporting the supposition that NC fine removal can promoted by simply reducing the pH and thereby reducing the particle surface charges. However, low turbidities were also achieved at pHs above 11. The average zeta potential at pH 11.8 was found to be approximately -25 mV, thus the observed enhanced particle settling at the high pHs cannot be attributed to reduced particle surface charges. The low turbidities achieved at the high pHs currently have no physical explanation.

Table 20. Jar test turbidity results (NTU) for pH adjustment-first trial (initial wastewater pH of 5.5).

Turbidity at:	pH 1.6	pH 2.5	pH 4.0	pH 5.5	pH 7.0	pH 9.0	pH 10.5
0 min.	112	112	112	112	112	112	112
30 min.	99	103	109	109	110	109	110

Table 21. Jar test turbidity results (NTU) for pH adjustment-second trial (initial wastewater pH of 7.7).

	pH										
Turbidity at:	2.0	2.5	4.0	5.0	7.0	9.0	10.0	10.5	11.0	11.5	11.8
0 min	530	530	530	530	530	530	530	530	530	530	530
30 min	26	23	150	476	527	520	510	38	8.2	3.0	2.0

In summary, the jar test experiments showed that: (1) a highly cationic polymer coagulant could effectively remove NC fines from the wastewater; however, the polymer used was found to react with NC; and (2) it may be possible to enhance NC fine removal by reducing the wastewater pH and thus reducing the particle surface charge; however, given the variability in experimental results, this possibility needs further investigation.

NC Slurry Settling Tests

Table 22 shows the results of the NC slurry settling tests. The zone settling velocities of the poacher tub, blender tub, and wringer tub NC slurries were observed to range from 0.66 cm/min to 2.31 cm/min. These settling velocities were undoubtedly inversely related to the slurry solids concentrations. The NC slurry released to the beater house dewatering tub from the dewatering box was found to be relatively dilute; consequently the NC particles settled in discrete flocs did not exhibit zone-type settling.

Table 22. Nitrocellulose slurry settling test results.

NC Slurry Sample	Settling Velocity (cm/min)
Beater tub 4-Pulp	17.8 **
Beater tub 4-Cotton	22.3 **
Poacher tub-Pulp before 2nd boil	0.93
Poacher tub-Pulp before 3d boil	0.74
Poacher tub-Pulp before 4th boil	0.97
Poacher tub-Cotton before 2nd boil	0.91
Poacher tub-Cotton before 3d boil	1.11
Poacher tub-Cotton before 4th boil	2.31
Blender tub-Pulp	0.66
Blender tub-Cotton	0.73
Wringer tub-Pulp	0.72
Wringer tub-Cotton	0.89

**The beater tub NC slurry exhibited flocculent-type settling. The remaining samples exhibited zone-type settling.

6 Development of Pollution Prevention Ideas

Pollution Prevention Ideas

By this field study at the RAAP, in addition to physical characterization of NC fines and NC containing wastewater described in above sections, pollution prevention (PP) ideas were developed. Discussion of the entire NC production process with the operators, foremen, and NC production engineers was a crucial part of PP idea development. NC is derived from common cellulose material such as cotton linters or wood pulp. The raw cotton linters come to the plant in bales while the wood pulp comes in rolls of paper-like product. The two different raw materials produce separate grades of NC. Of the two types of NC, four grades are made with the wood pulp and three grades are made with the cotton linters. In recent years, a greater emphasis has been placed on pollution prevention to improve our environment through recycling and to reduce the cost of wastewater treatment. In this study, several pollution prevention schemes were proposed to reduce the overall loss of NC fines from the NC production process wastewater. The minimization of NC fines in the wastewater could allow for smaller wastewater treatment system, less surplus of low grade pit cotton, lower operational costs of treatment and disposal, and higher productivity from the NC production line. The pollution prevention ideas included several operational/minor design changes to the NC production line, operational changes to the wastewater treatment system, and other system design modifications.

Most of the wastewater discharged to the poacher settling pits is generated during the decanting of the beater, poacher, blender, and wringer house operations. These decanting procedures involve lowering a decant pipe into the supernatant after the NC slurry has been allowed to settle. The tops of the pipes are fitted with decanting heads perforated with about 1/16 in. diameter holes. Approximately 3 to 5 percent of each initial load of NC is eventually lost to the poacher settling pits during the decanting operations. Significant quantities of NC are also lost to the poacher settling pits during the final wringing operations. Although most of the NC discharged to the settling pits is recovered as pit cotton (~80 to 95 percent), this is presumably of lower economic value than the NC subjected to normal processing. Thus it is desirable to minimize the amount of NC discharged to the settling pits. Furthermore, if the Army would decide to terminate the current practice of pit

cotton reuse, the Army must then develop methods for economic and effective disposal. The TSS concentrations in the final settling lagoon effluent discharged to the New River should also be minimized. Although RAAP complies with existing effluent limitations, it may be difficult for RAAP to meet more stringent standards with its current wastewater treatment processes. However, the new tube-settling basin may help to reduce the final effluent TSS.

Process Operational/Minor Design Changes

Boiling Tub House

During this step in the production line, the NC undergoes four different boils to begin the stabilization process. After each boil, approximately 5,800 gal (21.7 m^3) of water is drained through false bottoms to the acid settling pit at a rate of approximately 1,000 gal/min (3800 L/min) (Nietzold 1995). This drained wastewater is then replaced by filtered water to maintain product quality. The holes in the false bottoms are 1/16 in. (0.16 cm) in diameter, so for the first few minutes of draining the water, the pulp NC wastewater contains 26 mg/L of NC fines and the cotton NC wastewater contains 43 mg/L—as shown in Chapter 4. After 5 minutes, the TSS concentration in the draining pulp NC wastewater drops to approximately 16 mg/L and the cotton NC wastewater drops to 28 mg/L of TSS. The reduction in TSS in the wastewater is due to the formation of an NC mat on the false bottom. This mat further strains the NC fines from the drained wastewater. If the drained wastewater was recycled for 5 minutes until a sufficient mat of NC formed, roughly 0.19 kg of pulp NC fines and roughly 0.29 kg of cotton NC fines could be saved per draining. The wastewater is drained after each boil; therefore, 0.76 kg of pulp NC and 1.16 kg of cotton NC could be saved per tub. This option could be implemented by installing 3,800 L/min (1,000 gal/min) pumps at the drain pipes, which receive the false bottom effluent and recycling the water back to the appropriate NC slurry feed pipe. After the final boil, the water in the tub is completely drained.

Poacher House

In this step of the production process, the NC slurry undergoes several alkaline boiling cycles. To begin the process, the NC slurry load from the beater house is equally divided into three poacher tubs. Immediately on loading the NC slurry, approximately 22 m^3 (0.9 m deep) of water is decanted off the top of each tub to prevent water from boiling out of the tubs. The decanting occurs relatively soon after the NC is loaded to the tubs, and large quantities of NC fines are lost in this operation. A period for NC fine settling before the initial decanting would reduce

the concentrations of NC fines in the decanted wastewater. To determine the settling time needed and approximate TSS reduction in the wastewater, typical settling velocities of the NC particles must be found. Table 22, Chapter 5 (p 58), shows the results of NC slurry tests. Using a settling velocity of 0.9 cm/min for both types of NC, a 1-hour settling time would result in a TSS reduction of 40 percent in the decanted wastewater. The tubs are decanted for 1 hour, which results in a decant flow rate of 370 L/min (about 100 gal/min) (Nietzold 1995). This results in a savings of approximately 4.0 kg of pulp NC and 8.0 kg of cotton NC per three-tub load. Another alternative for the reduction in NC fine mass loading on the poacher settling pit would be to divide each NC slurry load from the beater house into four poacher tubs instead of three. With lower volumes in each tub, the initial decanting prior to the first boil would be unnecessary. The NC fines saved by implementing this option would be approximately 10.0 kg of pulp NC and 20.0 kg of cotton NC per three-tub load.

Blender House

In the blender house, different types of NC are blended together to achieve the required nitrogen content and solubility. On loading the blender house tubs, approximately 0.9 m (3 ft) of water is decanted before blending. Large amounts of NC fines are discharged to the poacher settling pit from this process. From Table 22, the NC particles have a settling velocity of 0.66 cm/min for pulp NC and 0.73 cm/min for cotton NC. Typical values for TSS in the blender house are approximately 400 mg/L for both pulp and cotton NC (Tables 2 and 3). With a 1-hour settling time, approximately 44 percent of the pulp NC and 49 percent of the cotton NC TSS could be reduced. This results in a savings of 3.9 kg of pulp NC and 4.3 kg of cotton NC per tub.

The NC particles in the blender house vacuum drum tail water tended to be larger and consequently settleable. While a reliable value for the flow rate associated with vacuum drum tail water was not available, it is unlikely that this wastewater stream constitutes a significant source of NC loading to the poacher pits given its relatively low TSS concentrations. However, NC recovery from the blender house vacuum drum tail water could possibly be achieved by installing a decanting device similar to those for the various NC processing tubs.

Wringer House

The NC is separated from the water in the wringer house, which employs basket centrifuges to perform the solid-liquid separation. During the wringing operations, the NC slurry is sent to a series of centrifugal wringers where the slurry is

dewatered and the final NC is produced. The permeate from the centrifuge screens contains very high concentrations of cotton NC fines (3600 mg/L) immediately after the screens are cleaned (Table 3). The concentration of cotton NC fines in the permeate when the screens have been caked with an NC mat was approximately 30 mg/L. Therefore, a simple method to drastically reduce the NC fines in the wastewater from 3600 to 30 mg/L would be to recycle the permeate for 30 seconds to a few minutes until the screens had been caked with NC. For this period, the centrifuges revolve slowly and each load (965 L of NC slurry) is dewatered in 4 minutes (Nietzold 1995). The permeate could be captured in a relatively small tank in the wringer house (1200 to 1900 L) and pumped back to the wringer receiving tubs. The cost of implementing this option would be minimal and approximately 0.4 kg of NC fines could be saved during each clean screen load. There are 80 clean screen loads per batch of NC; therefore, implementation of this option would save 34.4 kg of cotton NC fines per cotton NC batch (Nietzold 1995). Typically, the pulp NC fines concentration in the wastewater is between 25 and 50 percent of the cotton NC fines concentrations. Therefore, an approximate savings of 8 to 16 kg of pulp NC fines could also be saved per pulp NC batch.

Poacher Settling Pit

The poacher settling pit receives NC fines wastewater from the beater, poacher, blender, and wringer houses. The settling pit was designed to allow sufficient detention time for the sedimentation of the suspended NC fines; at present, operation is very inefficient at removing the NC fines in the wastewater. The main reason for the problems associated with the settling pit is the tremendous volume of settled NC buildup in the basin. Approximately every 3 months, the settled pit cotton rises above the water level (Nietzold 1995). Only then is the pit cotton removed. This is due to the lack of storage facilities for the pit cotton before its reuse. With the massive quantity of settled solids in the poacher settling pit, its efficiency is drastically reduced. The solids are easily resuspended and the actual detention time of the settling pit is much lower than the theoretical detention time. During present operation, the poacher settling pit removal efficiency approaches zero when the accumulated solids reaches a sufficiently high level in the settling pit. One suggestion to increase NC fine removal efficiency in the settling pit is to implement a more regular schedule for removing settled solids; twice monthly would be sufficient to keep the accumulated solids from causing significant removal problems.

Good Housekeeping

The amount of daily wet pit cotton volume was much larger than estimated NC quantity and was an indicator that NC fines or large fibers came from other than normal decanting processes; for example, from cleaning operation or accidental spill. Shortly after the sampling survey, a large amount of NC was noted to be accumulating in the poacher pit, much to the dismay of one of the operators. The source of the excessive NC loading may have been due to an upset caused by a switch in manufacturing lines. There is a need to develop an in-house pollution prevention strategy to eliminate accidental/avoidable discharge of NC into waste system.

Inventory Process Water Flow Rates and TSS Concentrations

Accurately determining the amounts of NC lost to the settling pits from each production process is currently quite difficult due to the uncertainty and variability in the process water flow rates and TSS concentrations. Better overall process control could be attained by metering water use and periodically measuring the TSS concentrations in the various wastewater streams.

Savings From Operational Changes

Table 23 shows that the implementation of the waste minimization ideas could save approximately 1.7 kg of pulp NC and 3.5 kg of cotton NC per metric ton of NC processed. Assuming 22,700 kg/day NC production with 65 percent pulp NC and 35 percent cotton NC base on actual data at the time of study, savings would total 25 kg pulp NC per day and 28 kg cotton NC per day. With the current NC production costs of $5.65 per kg pulp NC and $6.26/kg cotton NC, the total daily savings after waste minimization would be $316. Because the recovered NC is directly added to the production volume, the virgin NC price was used. Without the PP efforts, the

Table 23. NC fines saved by operational changes.

Operational Change	Pulp NC	Cotton NC
Initial false bottom effluent recycling in boiling tub house	0.08*	0.09
Install baffle and diffuser in beater house	N/A**	N/A
Initial settling of slurry in poacher house	0.40	0.60
Initial settling of slurry in blender house	0.39	0.32
Initial centrate recycling in wringer house	0.86	2.5
Total	1.7	3.5

* Unit: kg NC fines saved / metric ton NC produced
**N/A: data not available

NC will end up in the pits; recall that the price of pit cotton is much cheaper than virgin NC. Based on a production year of 260 days, the annual savings would be approximately $82,000 (Nietzold 1995). The implementation costs for the operational/minor design changes will range from a few thousand dollars to a few tens of thousands of dollars. The payback periods appear within 2 years.

Major Improvement

Motive Water Reduction From Acid Boiling Tub

To transfer the NC solids in the boiling tubs to the beater house, the operators open a suction drain on the false bottom and wash the NC solids into the drain with two fire hoses in an operation called cutting. This operations lasts between 3 and 4 hours depending on the operator and uses approximately 1000 gal (3800 L) of water per minute (Nietzold 1995). A less wasteful method for removing the NC would be to pump water into the tubs until enough water was available for pumping the solid NC. Currently, a solids content of 1 to 2 percent is produced during the cutting operation, and a solids content of 5 to 10 percent can be transferred to the beater house using the existing pumps (Nietzold 1995). At 10 percent solids, 100,000 L of water would be needed to transfer one tub of pulp NC and 136,000 L of water would be needed to transfer one tub of cotton NC; the cutting operation uses about 800,000 L of water to transfer the same mass of both cotton and pulp NC.

It is proposed that agitators mix the water and NC until a 10 percent solids slurry is produced. This slurry could then be pumped to the beater house with the existing suction line. Unlike other tubs in the NC production line, the boiling tubs do not have agitators. This is probably due to the acidic nature of the contents (pH ~2) and the high operating temperatures (98 °C). However, with a careful selection of material, agitators or hydraulic jet cutter could be installed. This would significantly reduce the volume of filtered water used in the boiling tub house, which would reduce the volume of water decanted in subsequent operations. With less water decanted from each operation, the mass loading of NC fines to the poacher settling pit will decrease. If implemented, wastewater generation could be reduced by 700,000 L per pulp NC batch and 664,000 L per cotton NC batch. Currently, the NC production line produces 3,500,000 L/day of wastewater with approximately 5 percent of the total NC produced lost as NC fines in the wastewater (Chapter 4). If the total wastewater flow were reduced by 87.5 percent for pulp NC wastewater and 83 percent for cotton NC wastewater, then 650 kg of pulp NC fines and 330 kg of cotton NC fines could be saved per day of production from this waste minimization option alone. This would result in substantial savings.

Install Microfiltration/Ultrafiltration Units

A highly effective (but costly) method of removing and recycling NC fines from the various decanted tub supernatants and final wringer centrate would be to install microfiltration units prior to the poacher settling pits. Previous pilot-scale studies (Kim et al. 1995) showed that NC fines could be almost completely removed from DeLaval centrifuge effluent or poacher pit effluent using microfiltration, but that this technology was limited in its application since large NC particles (>100 µm) obstructed the filtrate flow rate through the microfiltration membranes. However, it was proposed that this problem could be circumvented using rotary vacuum filters to first remove the larger particles. While installing rotary vacuum filters and microfiltration units would incur high capital costs, these could potentially be offset by eliminating the necessity of using the DeLaval centrifuges and perhaps by allowing for the resulting high quality effluent to be recycled as process water (although high salts concentrations could possibly prohibit this). Also, note that the high temperatures of the decanted poacher pit supernatants (typically around 77 °C) exceed the maximum operating temperature of the tested microfiltration (MEMTEC's* hollow fiber) units, and thus heat exchangers would have to be installed if this type of microfiltration were to be used. However, the heat exchangers could potentially be used to preheat the water used to wash the NC between boils at the poacher house. A heat exchanger may not be needed if ceramic or stainless microfiltration is used. Additionally, it is recommended that off-the-shelf prefiltration systems be evaluated and effectively adopted.

Microfiltration/ultrafiltration can be used for beater house, blender house, and wringer house effluent after the process change/minor modification for pollution prevention in the previous sections is implemented. An appropriate prefiltration system must be selected for successful use of microfiltration/ultrafiltration systems. Recently, bench scale evaluation was conducted to separate NC fines from process water comparing a dozen different microfiltration/ultrafiltration membranes. It was found that pore size of 100K molecular weight cut off, hydrophilic, cellulose acetate membrane performed best in terms of minimum irreversible fouling (Kim, Clark, and Lee 1996).

Design Change for Poacher House Settling Pit

The existing poacher house pit serves three purposes: (1) as a receiving and sedimentation basin for process water from the beater house, poacher house, blender

* MEMTEC America (MEMCOR), 9690 Deerco Rd., Suite 700, Timonium, MD 21093, tel: 410/560-3000.

house, and wringer house, (2) as an inlet for DeLaval centrifuges, and (3) as storage for concentrated NC from DeLaval centrifuges.

Installation of a continuous sludge removal mechanism should be considered in the poacher house settling pit. With a more frequent settled solids removal process, a pit cotton storage facility should be built. In 3 months, approximately 528 m^3 of wet pit cotton is generated every month. Therefore, using a continuous settled solids removal mechanism should generate approximately 6 m^3 of wet pit cotton every day. A storage tank with a 3-month detention time would allow sufficient time for the pit cotton to be reprocessed or properly disposed. This NC pit cotton storage capacity will prevent continuous feeding of some NC fines to centrifuges. With a new pit cotton storage facility, the poacher house pit would be able to serve as a setting basin. Consequently, solids loading to DeLaval centrifuges will be substantially reduced.

Disconnection of Hill Top Tank and Acid Boiling Tub House Pit

The original design concept was to pump the centrate of DeLaval centrifuge to Hill Top Tank and use this slightly alkaline centrate for neutralizing the highly acidic acid boiling tub pit water. However, when water from Hill Top Tank was discharged to acid boiling tub pit, NC fines in the pit tended to resuspend and overflow to the neutralization basin. Furthermore, accumulated NC fines cause a disposal problem. It is recommended that Hill Top Tank and the acid boiling tub pit be disconnected. The centrate from DeLaval centrifuge will directly or via Hill Top Tank be discharged to a neutralization basin or a final lagoon.

New Decanter

A less costly but probably less effective alternative to microfiltration may be to design new decanter heads that would prevent the discharge of the NC fines in the first place. However, the particle size distribution data showed that the NC particles in the various tub supernatants were predominantly below 10 μm. If decanting heads with filter screens were adapted to prevent these small particles from escaping, the decant flow rates would undoubtedly drastically decrease due to clogging. However, it may be possible to overcome this problem by designing a decanter with a self-cleaning apparatus, rotary screen, or stainless steel spiral coil filter.

Savings From Major Improvement

To develop cursory savings data from the implementation of major improvements to pollution prevention efforts, the following assumptions were made:

- 500-2000 lb/day of NC fines are generated in washwater (assume 1250 lb/day generation)
- Reuse of pit cotton for M14 propellant will be prohibited in the near future
- 80 percent of NC is recovered by pollution prevention
- Assume 260 working days/year
- Virgin NC price is $2.72/lb
- Annual savings will be about $1.4 million
- Assuming implementation costs of about $4 million, the payback period will be within 3 years:

$$\$2.72/\text{lb} \times 1250\ \text{lb/day} \times 260 = \$1.4\ \text{million}$$

7 Summary and Recommendations

NC Fines Characterization

Separation of NC fines from wastewater is not a simple process because particle sizes are small and vary widely. This study closely analyzed physical characteristics of NC fines to facilitate development of an NC separation technology for RAAP to help the plant to continue operations and maintain environmental compliance. This characterization data also provided a framework for pollution prevention of NC fines at RAAP.

This study obtained PSD, TSS, turbidity, zeta potential (particle surface charge), conductivity, and pH measurements for the various NC production wastewater streams discharged to the settling pits (i.e., boiling tub, beater, poacher, blender, and wringer houses), as well as from the wastewater treatment processes (i.e., settling basins, DeLaval centrifuge, recovered water tank, neutralization basin, and final settling lagoons). These measurements will help RAAP engineers in developing effective NC fine removal processes in the future. In addition, this study estimated the relative amounts of NC lost to the settling pits from each NC purification process (boiling tub, beater, poacher, blender, and wringer houses) and compared these estimates to previous NC mass balance studies. Jar tests were conducted to assess the feasibility of removing NC fines from the production wastewaters by coagulation and flocculation using both a cationic polymer and simple pH adjustments.

Particle Size Distributions

The PSD measurements were obtained using an automated Brinkmann PSA. This instrument allowed quick and simple PSD measurements. However, it was found that the PSA yielded unreliable PSD results for the NC wastewater samples with low TSS concentrations. In addition, the PSA method is based on the assumption that all detected particles are spherical. This is not strictly applicable to NC particles, since micrographs have shown them to be irregularly shaped. Despite these problems, it is nevertheless believed that the PSD results obtained in this study still provide a good indication of the relative distribution of NC particle sizes in the various NC production wastewater streams. Note that the PSD results

obtained in this study are based on total volume, whereas the PSD results for previous studies were based on total mass.

The NC particles in the poacher, blender, and wringer tub supernatant samples were found to be predominantly below 10 μm in size (>80 percent), while the NC fines in the blender house vacuum drum tail water and final wringer centrate samples were widely distributed from zero to >100 μm. The larger particle sizes in the vacuum drum tail water and wringer centrate can probably be attributed to these wastewater streams not being settled to remove solids before being discharged to the poacher pits. The NC particles in the beater house dewatering tub samples were found to be predominantly below 10 μm (greater than 80 percent) for the pulp NC supernatant, but to be widely distributed from zero to 100 μm for the cotton NC supernatant. The PSD results for the poacher settling pit inlet and outlet samples were widely distributed—from zero to >100 μm, the larger particle sizes probably being attributable to the unsettled wringer centrate and vacuum drum tail water wastestreams, and to the practice of discharging the DeLaval centrifuge backwash water back into the poacher pits. No reliable PSD results were obtained for the wastewater from the boiling tub drain, settling basin 3054, the boiling tub settling pit, the DeLaval centrifuge centrate, the neutralization basins, or the final settling lagoon due to very poor reproducibility in replicate analyses attributable to low TSS concentrations. However, the boiling tub drain, settling basin 3054, and boiling tub settling pit wastewater samples were all very clear with small amounts of large settled particles, indicating that the NC particles were on average quite large (e.g., >100 μm). Note that the boiling tub settling pit that was sampled during this study was not receiving effluent from the recovered water tanks; if it had been, there would have been a greater ratio of smaller NC particles.

PSD measurements for various NC production wastewaters were also previously obtained in a Hercules (1992) study. This study complements the Hercules study in that the Hercules study obtained PSD results for several locations for which results were not obtained in this study and vice versa. The Hercules study found that 87 percent of the NC particles in the DeLaval centrifuge centrate, 64 percent of NC particles in the neutralization basin influent, and 64 percent of the NC particles in the settling lagoon effluent were below 44 μm. This study did not obtain reliable PSD results for these locations due to the low TSS concentrations. Comparing the boiling tub and poacher settling pit PSDs, for which results were obtained in both studies, revealed some differences. The Hercules study found the NC particles in the boiling tub settling pit wastewater samples to be predominantly below 44 μm, but this study found the opposite. This difference can probably be attributed to the fact that the boiling tub settling pits received recovered water tank effluent in the previous study, but not in this study. A comparison of the poacher

settling pit effluent PSD results showed that the fraction of NC particles below 44 µm was found to be greater in the Hercules (1992) study than in this study (90 versus ~60 percent).

TSS Concentrations

The TSS analyses showed that, in general, the TSS concentrations in the boiling tub house drain wastewaters were fairly low (0 to 43 mg/L), while the TSS concentrations in the beater, poacher, blender, and wringer house supernatant wastewaters were fairly high (27 to 601 mg/L). The greatest TSS concentrations for the boiling tub drain wastewater were observed in samples collected just after opening the drain; this is believed to be a result of the formation of a mat of NC at the orifices in the boiling tub false bottoms that soon prevents the discharge of additional NC. The TSS concentrations of the various tub supernatants that had been settled approximately 1 hour ranged from 108 to 601 mg/L, while the TSS concentrations in tub supernatants that had been allowed to settle for more than 1 day were significantly lower, ranging from 81 to 155 mg/L. One potential explanation for this reduction in TSS with longer settling times is that NC fines may be kept in suspension while the NC slurry is still cooling due to turbulence caused by temperature gradients; however, once the NC is completely cooled, the supernatant may become more quiescent.

The TSS concentrations in the wringer centrate during a loading of a clean screen were high (385 mg/L for pulp NC and a very high 3,660 mg/L for cotton NC), but were much lower during the actual wringing process and during a loading of a caked screen (<120 mg/L). Obviously, the existence of a layer of NC on the wringer screens helps to prevent the loss of NC during the wringing process. The TSS in the poacher settling pit inlet samples ranged from 53 to 250 mg/L, while the outlet samples ranged from 107 to 171 mg/L. It should be noted that the practice of discharging the DeLaval centrifuge backwash water back into the poacher settling pits probably contributed to the high poacher pit outlet TSS concentrations. The TSS concentrations in the DeLaval centrifuge centrate samples ranged from 4 to 17 mg/L. The TSS concentrations in the wastewater from settling basin 3054, the boiling tub settling pits, and the final settling lagoon were generally below 10 mg/L. The TSS for the neutralization basin effluent samples were generally higher than for the influent samples (~16 mg/L versus ~8 mg/L) due to the formation of calcium sulfate and other precipitates from the addition of lime.

The TSS measurements obtained in this study were compared to previous studies (Hercules 1992 and 1993). Comparing this study to the Hercules (1992) study (which only analyzed samples from the settling pits, DeLaval centrifuges,

neutralization basins, and final settling lagoons) showed that the Hercules study found somewhat higher TSS concentrations for all the wastewater treatment locations. It is possible that the lower TSS concentrations found in this study resulted from manufacturing line-A-B being switched over to line-C, causing lower overall NC production rates during the sampling period. Comparing this study to the Hercules (1993) study (which only analyzed samples from the boiling tub, beater, poacher, blender, and wringer houses) showed that the two studies found comparable TSS concentrations for the poacher, blender, and wringer house wastewaters. However, the Hercules (1993) study found somewhat higher TSS concentrations for the boiling tub drain wastewater, and much lower TSS concentrations for the beater house dewatering tub supernatant (~4 mg/L versus ~110 mg/L).

Turbidities

The turbidity analyses showed that wastewaters from the boiling tub drain, DeLaval centrifuge centrate, settling basin 3054, boiling tub settling pit, and final settling lagoon all had turbidities below 10 NTU. The beater, poacher, blender, and wringer tub supernatant samples all had very high turbidities, ranging from several hundred to >1000 NTU. The wringer centrate during clean screen loading had turbidities of several hundred NTU, but the caked screen loading samples had turbidities of below 15 NTU.

Chemical Characteristics

The electrophoretic mobility analyses showed that the fines in the NC processing wastewaters had average zeta potentials (surface charges) ranging from -16 to -34 mV, and thus could be characterized as having moderately high to very high surface charges. No zeta potential results were obtained for the boiling tub, settling basin 3054, boiling tub settling pit, neutralization basin, or settling lagoon samples, again due to very poor reproducibility in replicate analyses attributable to low suspended solids concentrations.

The pHs of the NC wastewaters were generally near neutral (6 to 8), except for wastewaters from the boiling tub drain, settling basin 3054, the boiling tub settling pit, and the neutralization basin influent, which all ranged from pH 1 to 3. Similarly, the conductivities of the neutral NC wastewaters were all below 800 µmho/cm, while the low pH wastewaters from the boiling tub drain, settling basin 3054, boiling tub settling pit, and the neutralization basin influent had conductivities ranging up to 30,500 µmho/cm.

Mass Balance Calculations

The masses of NC discharged to the settling pits from the five processing operations (boiling tub, beater, poacher, blender, and wringer houses) were estimated using the TSS measurements made in this study and water balances approximated in a previous study (Hercules 1993). Significant NC losses were estimated for the beater, poacher, blender, and wringer houses, while losses from the boiling tub house were found to be minimal. It was estimated that between 3 and 6 percent of each initial load of NC is lost to the settling pits, but that approximately 95 percent of this is recovered as pit cotton. Thus, the amount of each load of NC ultimately lost to the final settling lagoons was estimated to be only approximately 0.25 percent.

The mass balance estimations above were found to be quite comparable to mass balance estimations made in the 1993 RAAP study, with the exception that NC losses from the beater house were estimated to be 30 times greater in this study than in the 1993 study. The Hercules (1993) study estimated slightly lower NC recovery rates for the settling pits (~79 versus 95 percent), and consequently a slightly greater ultimate loss to the final settling lagoons (~0.90 versus 0.25 percent). It should be noted that the differences in the mass balance estimations for the two studies only reflect differences in measured TSS concentrations since the same flow approximations were used.

Jar Tests

The jar tests conducted with the Rhone-Poulenc C-4450 cationic polymer showed that the polymer was very effective in promoting coagulation and settling of the NC fine particles in the poacher settling pit wastewater, producing perfectly clear (zero NTU) wastewater after treatment. However, a compatibility test showed that the polymer reacted with NC. This raises questions as to whether the polymer can be used to remove NC fines from the RAAP wastewaters, and rules out recycling NC fines that have been settled out using the polymer. The jar tests conducted using only pH adjustments suggested that it may be possible to enhance NC fine settling rates by reducing the wastewater pHs and thus reducing the particle surface charges; however, variability in the experimental results indicated that this possibility would have to be investigated further.

Pollution Prevention Ideas

This study developed pollution prevention ideas based on discussion with plant operators and engineers and extensive data search. The pollution ideas consisted

of operational changes and minor design modification combined with several other improvements. It is estimated that the operational changes/minor design modification to the NC production line presented in this report can reduce the total amount of NC fines in the wastewater by approximately 53 kg per day based on production of 22,700 kg/day of NC, yielding an estimated cost savings of $82,000 annually.

A cursory cost estimate shows that the other major improvements suggested by this study can together save more than $1 million per year. However, a detailed cost analysis was beyond the scope of this report. Operational process/minor design modifications were recommended at the boiling tub house, poacher house, blender house, wringer house, and poacher settling pit. Good housekeeping was also added as an important element. Major improvements included motive water reduction at acid boiling tubs, installation of microfiltration/ultrafiltration with proper pre-filtration system, design change of poacher house settling pit, disconnection of Hill Top Tank from the acid boiling tub pit, and development of a new decanter.

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